I. S. Dmitriev

Molecules Without Chemical Bonds

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Молекулы без химических связей

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Essays on "Chemical Topology"

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Some ten years ago only the few were aware of the existence of molecules without chemical bonds. Nowadays a new scientific discipline, chemical topology, appeared to study them. This science has succeeded in predicting and producing many remarkable chemical compounds (e.g. catenanes whose molecules are interconnected like links of a chain), in defining the electronic structure of molecules more precisely, and so on.

The complicated concepts of chemical topology are presented here in a clear and comprehensible form.

The booklet is intended for teachers and university and high-school students majoring in chemistry and mathematics.

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Author's preface

In recent chemical literature more and more often one
comes across such terms as "topology of a molecule",
"topological properties", "topological bonding", etc. Broad-
ly speaking, topology is a branch of mathematics deal-
ing with the phenomenon of continuity. A more detailed
definition would require from the reader a more pro-
found knowledge of many complex mathematical concepts.
This book, however, is designed primarily for a chemist.
Besides, it is a popular science book (of course, if one
regards as popular science not only books of what-chemis-
try-makes-of-timber type). For this reason we shall give
here only the most essential data on topology.

High-school geometry, as a rule, looks into those prop-
erties of geometrical figures that are associated with
the notions of length, angle, area, and volume. These
properties of figures are called metric. In addition, there
are properties of figures that are independent of their size
or shape; for instance, stretching, shrinking, bending,
and twisting neither bring various points of the figure
into contact, nor induce any ruptures in it. One calls
such transformations *homeomorphic*. The transformation
of a doughnut into a mug shown in Fig. 1 (p. 8) is homeo-
morphic. A juggler in Fig. 2 (p. 9) removing the vest
without taking off the jacket also performs a homeomor-

phic transformation with the vest. The properties of bodies remaining invariable in homeomorphic transformations are examined by topology and called topological. The shape and the size of a figure are of no importance in topology.

Metric parameters of molecules, such as equilibrium distances between nuclei, valence angles, etc., are closely
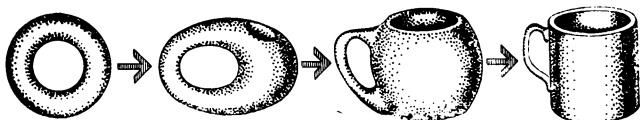

Fig. 1

connected with their electronic structure. As will be shown later, however, some molecular properties depend weakly, if at all, on geometry and are determined essentially by the way the atoms are connected to one another, i.e. by topology. For example, both hydrogen atoms in a water molecule form covalent bonds with the oxygen atom and are not bonded together.

An important point should be raised here, though. Strictly speaking, the term "topology of a molecule", as well as other related terms, cannot be regarded as wholly appropriate since chemical structures are discrete, and it would be more competent to consider a molecule in terms of the graph theory. Surely, a graph can be defined as a topological object, but the methods of the graph theory are not topological for the most part. Nevertheless, chemists often use the above-mentioned, not very rigorous terms not only out of the vainglorious urge to show off, but primarily to stress the fact that some properties of a molecule are independent of its geometry and the nature of the chemical bond. In the same sense, we shall also be dealing here with chemical topology.

It should be noted that this book, both in its structure and in its content, is in many respects logically related to our earlier booklet: I. S. Dmitriev, *Symmetry in the World of Molecules*, Mir Publishers, Moscow, 1979. This relation is not accidental since both topology and symmetry of molecules furnish a valuable qualitative and semi-quantitative complementary information about their structure and properties.

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Fig. 2

Chapter One   # Approximation
to Accuracy
and Accuracy
of Approximation

The Value of a Decimal Place

Modern quantum chemistry has developed diverse methods of calculating molecules. Usually these methods are divided into three groups:

(1) comprehensive nonempirical *ab initio* calculations involving all electrons of a system; only the values of internuclear distances, if at all, are borrowed from experimental data;

(2) semi-empirical semiquantitative calculations in which only valent electrons (and sometimes even not all of them) are taken into account; in this case some of the integrals are discarded and others are approximated by a special selection of parameters whose values are borrowed from experimental data;

(3) qualitative methods of analysis based on the fundamental concepts of quantum chemistry, the symmetry considerations, and, more and more often recently, on the topological methods.

Surely, all three approaches to the problem of electronic structure of molecules are closely interrelated. The modern theory of chemical bonding, on the one hand, relies on the growing utilization of powerful computers enabling various systems of interest to a chemist to be calculated in greater detail, and, on the other hand, develops new qualitative methods, thus enriching itself ideologically.

We begin with a brief outline of some methods and approximations of quantum chemistry.

The LCAO MO method. The method of molecular orbitals (MO) dominates in modern quantum chemistry. The main idea of the method is that the electrons in a molecule are accommodated in definite MOs just as in an atom they

are accommodated in definite AOs, i.e. in accordance with the Pauli principle, the orbitals being usually filled as the energy of the MO grows.

Normally MOs are made up as *linear combinations of atomic orbitals* (LCAO) of atoms composing the system, i.e. are written in the form

$$\psi_i = \sum_{j=1} c_{ji}\varphi_j, \tag{1}$$

where i is the number of the MO ψ; j are the numbers of atomic φ-orbitals; c_{ij} are the numerical coefficients defining the contributions of individual AOs into the given MO.

Such a way of constructing a MO is based on the assumption that an atom represented as a definite set of orbitals remains distinctive in the molecule.

The complete N-electron wave function of a molecule is represented in the form of the Slater determinant composed of the MOs:

$$\Psi(x_1, \ldots, x_N) =$$

$$= 1/\sqrt{N!} \begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \ldots & \psi_1(x_N) \\ \psi_2(x_1) & \psi_2(x_2) & \ldots & \psi_2(x_N) \\ \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \\ \psi_N(x_1) & \psi_N(x_2) & \ldots & \psi_N(x_N) \end{vmatrix}. \tag{2}$$

Electrons interchanged. When the many-electron function of a molecule is written in the form of a determinant, the fundamental antisymmetry principle (the Pauli exclusion principle) of quantum mechanics is satisfied. According to that principle an N-electron function must be antisymmetric, i.e. it must change sign whenever spatial and spin variables of any two electrons are interchanged:

$$\Psi(x_1, x_2, \ldots, x_i, \ldots, x_k, \ldots, x_N) =$$

$$= -\Psi(x_1, x_2, \ldots, x_k, \ldots, x_i, \ldots, x_N).$$

This is exactly the property that expression (2) possesses since any determinant changes its sign when its two rows, or two columns, are interchanged. (The readers themselves may easily check this in the case of a determinant of the second order.) It thus follows that each molecular spin orbital can accommodate not more than one electron and accordingly each molecular orbital can

accommodate not more than two electrons (with[)] opposite spins). Otherwise, two rows in determinant (2) become identical, and such a determinant with two identical rows (or columns) is always equal to zero. And what if the Slater determinant is equal to zero? This means that $\Psi(x_1, x_2, \ldots, x_N) \equiv 0$, i.e. the system in question cannot exist in such a state.

Thus we came to the conclusion that in the MO method the total (N-electron) wave function of a molecule is expressed via one-electron functions, that is, molecular spin orbitals which, in their turn, are expressed via atomic spin orbitals. Subsequently we shall be utilizing only MOs expressed in the LCAO form. Although the spin variables will not be taken into account, the Pauli principle will be obeyed.

In 1928 the British scientist D. Hartree suggested his method of calculating orbitals. In 1929 his approach was generalized by V. A. Fock who derived more general equations, putting to use the principle of antisymmetry.

Roothaan's equations. In 1951 using Fock's method the American physicist C. C. Roothaan worked out a system of nonlinear algebraic equations providing the AO coefficients of Eq. (1):

$$\sum_b (F_{ab} - \varepsilon_k S_{ab}) c_{bk} = 0, \tag{3}$$

where F_{ab} is the quantity specifying the contributions that various interactions (electron-electron, electron-nucleus, etc.) make to the energy of a molecule; since this quantity has a fairly complicated mathematical form, it is not presented here in an explicit form; S_{ab} is the orbital overlap integral; ε_k is the energy of the k-th MO. Equations of type (3) are called *secular*.

Let us compose the following column matrix from the coefficients of expansion of the i-th MO into the corresponding AOs:

$$\mathbf{c}_i = \begin{pmatrix} c_{i1} \\ c_{i2} \\ \vdots \\ c_{im} \end{pmatrix}.$$

Then Eq. (1) can be written in a compact form as

$$\psi_i = \varphi c_i,$$

where φ is the row of the AO:

$$\varphi = (\varphi_1, \varphi_2, \ldots, \varphi_m).$$

Assembling the columns c_i into the matrix C of $m \times n$ size (m is the number of AOs and n is the number of MOs), we can rewrite Eq. (1) in the form of a single matrix equality

$$\psi = \varphi C,$$

where ψ is the row of the MO:

$$\psi = (\psi_1, \psi_2, \ldots, \psi_n).$$

Then the Roothaan equations can be written in the matrix form:

$$FC = SC\varepsilon \qquad (4)$$

where F is the so-called Fock matrix composed of the elements F_{ab}; S is the overlap matrix; ε is the matrix whose diagonal elements specify the MO energies, all other elements being equal to zero.

Solution of the Roothaan equations calls for laborious computations which become more and more so as the basis broadens, i.e. the number of AOs increases. In the last two decades theoreticians have invented a great number of clever tricks in their attempts to find how to calculate molecules "the Roothaan way". However, the system of equations (4) turned out to be very tough to handle. Despite the ingenuity of researchers and the advancement in computer technique practical application of the Roothaan method is substantially limited by the size of molecular systems.

Finding a way out. Calculations can be considerably simplified by using approximation of the *zero differential overlap* (ZDO). The essence of this approximation is that the overlap of different AOs ψ_i and ψ_j is assumed to be equal to zero for any element $d\tau$ of the volume of a molecule:

$$\varphi_i \varphi_j d\tau = 0 \qquad (i \neq j).$$

Consequently, all overlap integrals also turn to zero:

$$S_{ij} = \int \varphi_i \varphi_j \, d\tau = 0$$

as well as many other integrals, including those which are the hardest to crack. Initially, the ZDO approximation was introduced as a postulate, and only later was it substantiated theoretically and its validity limits were set. Many varieties of the ZDO method are now extensively employed in quantum chemistry.

Cost of accuracy. At present with the appearance of the ZDO approximation that considerably simplifies calculations, theoreticians often prefer a semi-empirical approach in which most of the "troublesome" integrals are either neglected completely or expressed via the parameters found experimentally (orbital ionization potentials, electron affinity etc.). In this case the successful calibration of the empirical parameters can offset the loss in accuracy caused by various simplifications introduced into the Roothaan calculation method.

Today semi-empirical calculation methods provide a great deal of theoretical information about the electronic structure of chemical compounds. This preference for semi-empirical methods is primarily due to the following two factors.

First, nonempirical calculations consume much computer time which makes them more expensive.

Second, semi-empirical methods admit, as a rule, more readily, descriptive interpretation in terms of conventional chemistry.

While giving credit to these methods one should not forget their drawbacks, in particular, the lack of rigid criteria to assess their accuracy. According to the British scientist G. G. Hall, each theoretician has a semi-empirical method he believes in, but never trusts other semi-empirical methods.

Complexities of a Simple Method

The first and the simplest form of the molecular orbital theory was proposed by E. Hückel in 1931. Despite its simplicity (which is largely seeming, anyway) this method is still extensively used in theoretical chemistry to-

day in its various modifications, emphasizing once again the fact that the calculation methods cannot be unconditionally judged as the good ones or the poor ones for much depends on what is the system, which of its properties are studied, and what approximation is used. In quantum chemistry, as in other disciplines for that matter, it is important not only to attain the maximum possible accuracy of calculations, but also to choose the approximation most adequate for the given problem. It is relevant here to recall the words of the eminent French mathematician A. Poincaré: "The problem is not in what is the answer, the problem is in what is the question."

Because of its simplicity and limited computational requirements the Hückel theory was especially useful in the period before the application of computers to quantum-chemical problems (1930-mid1950s). However, since the 1960s the two opposite views concerning the Hückel theory have been advocated. One is that the days of this theory are numbered because high-speed computers and more sophisticated MO methods are now available. The other view is that there is still room for using the Hückel theory in organic chemistry, especially on a qualitative level as a guide for the chemists in planning and interpreting experiments. This latter opinion is consistent with the view that most experimental chemists prefer a "pencil-and-paper" method for their everyday research.

The Hückel method. In the Hückel molecular orbital method the Fock matrix (see Eq. (4)) is replaced by a certain "effective" matrix $\mathbf{H}$ whose elements H_{kj} are not explicitly specified.

Then each MO ψ_i is composed of N valence AOs of atoms in a molecule, i.e. is written in the LCAO MO form.

Frequently the secular equation defining the coefficients c_{ij} and the orbital energies ε_i is also derived with the use of the ZDO approximation. Then the equations of the Hückel method take the following form:

$$\sum_{j=1}^{j=N} (H_{kj} - \varepsilon_i \delta_{kj}) c_{ji} = 0 \qquad (5)$$

$$(k = 1, 2, \ldots, N),$$

where

$$\delta_{hj} = \begin{cases} 0, & \text{if } k \neq j, \\ 1, & \text{if } k = j. \end{cases}$$

Eqs. (5) have nontrivial solutions provided the secular determinant is equal to zero:

$$\det | H_{kj} - \varepsilon_i \delta_{kj} | =$$

$$= \det \begin{vmatrix} (H_{11} - \varepsilon_i) & H_{12} & \ldots & H_{1N} \\ H_{21} & (H_{22} - \varepsilon_i) & \ldots & H_{2N} \\ \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \\ H_{N1} & H_{N2} & \ldots & (H_{NN} - \varepsilon_i) \end{vmatrix} = 0. \qquad (6)$$

As has been mentioned, the matrix elements H_{hj} are not specified explicitly in the HMO method. They are treated as parameters whose values are determined from experimental data.

The same equations in a matrix form. Eqs. (5) and (6) can be written in a more compact form if one uses matrix notation. Thus, Eq. (5) in matrix form is

$$(\mathbf{H} - \varepsilon_i \mathbf{I})\mathbf{c}_i = 0, \qquad (7)$$

where $\mathbf{c}_i$ is a column matrix composed of the AO coefficients; $\mathbf{H}$ is a matrix composed of the elements H_{hj}; $\mathbf{I}$ is the diagonal unitary matrix.

Eq. (6) takes the following form in matrix notation:

$$\det | \mathbf{H} - \varepsilon_i \mathbf{I} | = 0. \qquad (8)$$

Overlap is allowed for. In the Hückel method the overlap integrals are usually discarded in calculations. But they can be taken into account. In this case Eqs. (7) and (8) take a somewhat complicated form:

$$(\mathbf{H} - \varepsilon_i \mathbf{S})\mathbf{c}_i = 0, \qquad (9)$$

$$\det | \mathbf{H} - \varepsilon_i \mathbf{S} | = 0.$$

However, account taken of the overlap integrals does not generally improve the calculations appreciably.

Maximum simplicity. So let us return to the simplest version of the Hückel method. We have not as yet mentioned still another simplifying assumption of this method: most of the matrix elements in Eq. (6) are assumed

to be equal to zero; the remaining elements are the diagonal elements H_{ii} called the Coulomb integrals and denoted by α_i and those nondiagonal elements H_{ij} ($i \neq j$) for which the indices i and j relate to the orbitals of the *chemically bonded nearest-neighbour atoms*. The nondiagonal matrix elements H_{ij} are called the *resonance* integrals and denoted by the symbol β_{ij}.

The Coulomb integral α_i defines the AO φ_i and, consequently, the atom to which this AO belongs; in this case $\alpha < 0$. The resonance integral β_{ij} defines the AOs φ_i and φ_j; in the case of finite internuclear distances R $\beta_{ij} < 0$.

In the HMO method the total energy of a molecule in the ground state is equal to the double sum of orbital energies:

$$E_{total} = 2 \sum_\mu \varepsilon_\mu \qquad (10)$$

(over occupied MOs)

The factor 2 reflects the fact that we consider a molecular system with closed electronic shell, that is, each MO accommodates two electrons with opposite spins.

Eq. (10) is obviously erroneous because in the one-electron approximation the total energy does not reduce, in fact, to the sum of the orbital energies, i.e.

$$E_{total} \neq 2 \sum_i \varepsilon_i$$

but differs from that sum by the value of the averaged interelectronic repulsion energy. The indicated drawback of the HMO method, as well as its other weak points, naturally limits the application of this method for the quantitative analysis of electronic structure of molecules, but it is quite acceptable for qualitative conclusions.

The HMO method proved to be most efficient in studies of conjugated and aromatic systems.

Properties of conjugated systems. Conjugation manifests itself in molecules in many ways. By formal definition, conjugated compounds are those which feature alternating

singleand multiple bonds, e. g. butadiene $CH_2=$ $=CH—CH=CH_2$ or benzene $\langle\!\langle \,\, \rangle\!\rangle$. As a rule, molecules of this kind exhibit a number of peculiar properties, primarily, higher thermodynamic stability. How much "higher"? Comparing to what? When higher stability of conjugated systems is discussed, chemists compare them to hypothetical systems possessing noninterfering localized multiple bonds. For instance, the heat of hydration of one double bond in a "real" butadiene molecule is less than the heat of hydration of ethylene, and the heat of combustion of butadiene is less than that of the hypothetical system with localized double bonds by appreciable (although small) value of 14.7 kJ/mol. In the case of benzene the respective difference is much higher and amounts to 155 kJ/mol.

Thus, the first characteristic of conjugated system is associated with their energy parameters, e.g. the energy of butadiene and benzene is lower than that of the respective classical structures.

The second characteristic of conjugated molecules is their inherent tendency to equalize the lengths of single and multiple bonds. For instance, whereas in ethane $R_{C-C} = 1.54$ Å and in ethylene $R_{C=C} = 1.34$ Å, the interatomic distances in butadiene are as shown below:

$$H_2C \overset{1.35\,Å}{=\!=\!=\!=} CH \overset{1.48\,Å}{\text{———}} CH \overset{1.35\,Å}{=\!=\!=\!=} CH_2$$
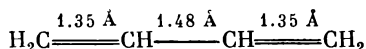
In benzene the lengths of all carbon-carbon bonds are equal to 1.397 Å.

Other characteristics of conjugated molecules can also be indicated: the shift of the UV absorption maximum of butadiene and other polyenes to the longwave region of spectrum as compared to ethylene, the lowering of ionization potentials, and so on. In short, there is much evidence pointing to the fact that the properties of conjugated systems are determined by the interaction of multiple bonds.

However, as will be shown in Chapter 4, not all formally conjugated systems possess the above-mentioned prop-

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erties, so that the definition of the term "conjugation" becomes rather difficult.

Note that most of theoretical concepts in chemistry are associated with a certain approximation and each approximation, in its turn, with the introduction of new notions whose physical meaning is often far from being clear. Among such notions are electronegativity, aromaticity, conjugation, hybridization, and others. Experimental chemists impart significant empirical meaning to those notions, and theoretical chemists manage to interpret various aspects of that meaning, more or less convincingly, using a certain model.

The Hückel approximation. One of the most popular models is the model of unsaturated molecules which is based on the *Hückel approximation**, or the approximation of σ-π-separability. The presence in conjugated systems of a symmetry plane coinciding with the plane of the nuclear skeleton of a molecule allows its MOs to be divided into two orthogonal groups, symmetrical (σ-MOs) and antisymmetrical (π-MOs) relative to the reflection in that plane. Consequently, one can consider the π shell of a molecule separately from the σ frame. In other words, in the π-electron approximation we consider not just valence orbitals but valence π orbitals.

In this case the σ frame is assumed to be conservative, in the sense that it is not polarized and its orbital energies are lower than those of the π shell. However, the non-empirical calculations demonstrated that the σ frame is not so much conservative as our ideas about that frame are. The σ electrons contribute substantially to the energy and appreciably to the polarizability of conjugated systems. Nevertheless, the π-electron approximation is quite acceptable in those numerous cases when qualitative and semi-quantitative results must be obtained. We should only remember that what we use *is* an approximation!

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* The Hückel approximation (not to be confused with the computational Hückel method!) is also called the π-electron approximation.

Calculations Without a Computer

Let us consider now a few examples of calculations of conjugated hydrocarbons by the Hückel method and in the Hückel approximation.

The first example: ethylene. In an ethylene molecule there are two π electrons forming one π bond between the carbon atoms. The corresponding π-MO can be represented as a linear combination of two $2p_\pi$ AOs of carbon atoms, φ_1 and φ_2:

$$\psi_i = c_{1i}\varphi_1 + c_{2i}\varphi_2.$$

To write the secular equation, one has to label the carbon atoms in an ethylene molecule:

$$\overset{1}{C} = \overset{2}{C}$$

and then to compose the determinant whose diagonal elements are all equal to $(\alpha - \varepsilon)$ and nondiagonal elements located at the intersection of the i-th row and the j-th column are equal to either β or 0 depending on whether the i-th and j-th atoms are chemically bonded (via a single or a multiple bond) or not. Then the following secular equation can be ascribed to ethylene:

$$\det \begin{vmatrix} \alpha - \varepsilon & \beta \\ \beta & \alpha - \varepsilon \end{vmatrix} = 0,$$

from which, by solving the determinant, we obtain:

$$(\alpha - \varepsilon)^2 - \beta^2 = 0.$$

This equation has two roots:

$$\varepsilon_1 = \alpha + \beta,$$
$$\varepsilon_2 = \alpha - \beta.$$

Now we can find the coefficients c_{1i} and c_{2i}. In our case Eq. (7) takes the form

$$c_{1i}(\alpha - \varepsilon_i) + c_{2i}\beta = 0.$$

Substituting into this equation first ε_1 and then ε_2 we get

for ε_1 $c_{11} = c_{12} = c$ and $\psi_1 = c(\varphi_1 + \varphi_2)$,

for ε_2 $c_{21} = -c_{22}$ and $\psi_2 = c(\varphi_1 - \varphi_2)$.

Then taking account of the condition for normalization of orbitals, we obtain $c = 1/\sqrt{2}$.

Thus, we finally get the following expressions for π-orbital energies and for π MOs of ethylene:

$$\varepsilon_1 = \alpha + \beta \qquad \psi_1 = 1/\sqrt{2}\,(\varphi_1 + \varphi_2),$$

and

$$\varepsilon_2 = \alpha - \beta \qquad \psi_2 = 1/\sqrt{2}\,(\varphi_1 - \varphi_2).$$

Since both parameters α and β are negative, the molecular orbital ψ_1 occupies a lower energy state than the orbital ψ_2: $\varepsilon_1 < \varepsilon_2$.

Figure 3 illustrates both MOs together with their squares. It can be seen from this figure that the MO ψ_1 is char-
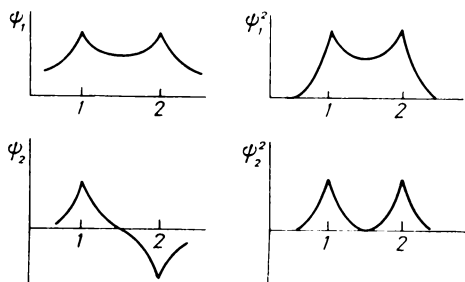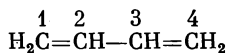

Fig. 3

acterized by a high electronic density between the nuclei whereas the MO ψ_2, and its square, turn into zero at a point located between the nuclei. Accordingly, the π MO ψ_1 is called the *bonding* (BMO) and the π MO ψ_2 *antibonding* orbital (ABMO).

The second example: butadiene. In the case of a butadiene molecule

$$\overset{1}{H_2C}=\overset{2}{CH}-\overset{3}{CH}=\overset{4}{CH_2}$$

the HMO method provides the following secular equation:

$$\det \begin{vmatrix} \alpha - \varepsilon & \beta & 0 & 0 \\ \beta & \alpha - \varepsilon & \beta & 0 \\ 0 & \beta & \alpha - \varepsilon & \beta \\ 0 & 0 & \beta & \alpha - \varepsilon \end{vmatrix} = 0. \qquad (11)$$

For the sake of convenience we shall introduce the designation

$$x \equiv \frac{\alpha - \varepsilon}{\beta}.$$

Then Eq. (11) takes the form

$$\det \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0.$$

Solving this determinant, we easily obtain the biquadratic equation

$$x^4 - 3x^2 + 1 = 0$$

whose roots are

$$x_{1,2} = -\frac{1 \pm \sqrt{5}}{2},$$

$$x_{3,4} = \frac{1 \pm \sqrt{5}}{2}.$$

Correspondingly, we obtain four energy levels (in the order of their increase):

$$\left.\begin{aligned} \varepsilon_1 &= \alpha + 1.618\beta \\ \varepsilon_2 &= \alpha + 0.618\beta \end{aligned}\right\} \text{ energies of bonding } \pi \text{ MOs,}$$

$$\left.\begin{aligned} \varepsilon_3 &= \alpha - 0.618\beta \\ \varepsilon_4 &= \alpha - 1.618\beta \end{aligned}\right\} \text{ energies of antibonding } \pi \text{ MOs.}$$

Spending some more time, we can obtain expressions for the corresponding four MOs*:

$$\psi_1 = 0.3717\ \varphi_1 + 0.6015\ \varphi_2 + 0.6015\ \varphi_3 + 0.3717\ \varphi_4,$$

$$\psi_2 = 0.6015\ \varphi_1 + 0.3717\ \varphi_2 - 0.3717\ \varphi_3 - 0.6015\ \varphi_4,$$

$$\psi_3 = 0.6015\ \varphi_1 - 0.3717\ \varphi_2 - 0{,}3717\ \varphi_3 + 0.6015\ \varphi_4,$$

$$\psi_4 = 0.3717\ \varphi_1 - 0.6015\ \varphi_2 + 0.6015\ \varphi_3 - 0.3717\ \varphi_4.$$

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* If a molecule possesses certain elements of symmetry, MOs are easier to calculate and classify using the group theory (see our book *Symmetry in the World of Molecules*).

From Fig. 4 it can be seen that the π orbital ψ_1 has no nodes and is strongly bonding, and the π MO ψ_2 has one node. The latter orbital bonds the atom C^1 with C^2 and
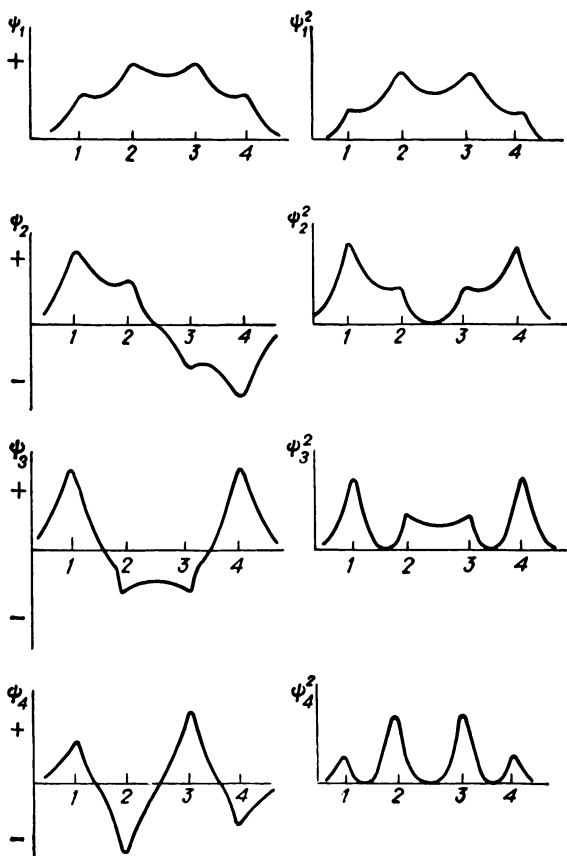

Fig. 4

the atom C^3 with C^4 loosening the bonding between the atoms C^2 and C^3. The bonding effected by this MO is weaker compared to that effected by the former MO. The π MO ψ_3 is a weak antibonding orbital which strengthens only the $C^2 - C^3$ bond. And finally, the antibonding π MO ψ_4 loosens all the three bonds,

Delocalization energy. To describe quantitatively the interaction of π bonds in conjugated systems, the concept of delocalization energy (resonance) E_D is frequently introduced. Usually it is defined as follows.

The delocalization energy E_D is the difference between the total π-electron energy of a given conjugated compound (E_{total}^{π}) and the energy of all localized bonds in that compound $(E_{total}^{\pi\ loc})$*.

For example, in butadiene four π electrons are accommodated in the two bonding MOs, ψ_1 and ψ_2, and the total π-electron energy of the molecule is

$$E_{total}^{\pi} = 2\,(\alpha + 1.618\beta) + 2\,(\alpha + 0.618\beta) = 4\alpha + 4.472\beta.$$

Assuming the π bonds to be noninteracting, we find that $E_{total}^{\pi\ loc}$ is equal to the double π-electron energy of ethylene, i.e.

$$E_{total}^{\pi\ loc} = 4\alpha + 4\beta.$$

Then the delocalization energy equals 0.472β. Since $\beta < 0$, the delocalization results in the lowering of the total energy of a butadiene molecule, i.e. increases its stability.

Polyene with N carbon atoms. In the general case of polyene with N carbon atoms forming a linear carbon chain $[CH_2(CH)_{N-2}CH_2]$ the secular equation takes the form

$$\det \begin{vmatrix} x & 1 & 0 & 0 & \dots & 0 \\ 1 & x & 1 & 0 & \dots & 0 \\ 0 & 1 & x & 1 & \dots & 0 \\ & & \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot & & \\ 0 & 0 & 0 & 0 & \dots & 1 \\ 0 & 0 & 0 & 0 & \dots & x \end{vmatrix} = 0$$

and its solution is given by the general formula

$$x_{\mu} = -2\cos\left(\frac{\pi\mu}{N+1}\right)$$

$$(\mu = 1,\ 2,\ \dots,\ N)$$

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* Somewhat different definitions that are sometimes given will not be discussed here.

or

$$\varepsilon_\mu = \alpha + 2\beta \cos\left(\frac{\pi\mu}{N+1}\right).$$

The AO coefficients in the expression for the k-th MO are found from the general formula

$$a_{\mu k} = \sqrt{\frac{2}{N+1}} \sin\left(\frac{k\pi\mu}{N+1}\right).$$

When the chain is closed. Using the Hückel method and the π-electron approximation, let us consider now the most typical aromatic compound, benzene. Repeating the arguments and the calculations presented above, we obtain the secular equation for benzene in the form

$$\det\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0.$$

Whence:

$$(x^2 - 1)^2(x^2 - 4) = 0$$

and

$$x_{1,2} = \pm 2, \quad x_{3,4,5,6} = \pm 1.$$

Correspondingly, we get six energy values of π-MOs*:

$$\varepsilon_1 = \alpha + 2\beta; \quad \varepsilon_2 = \varepsilon_3 = \alpha + \beta;$$
$$\varepsilon_4 = \varepsilon_5 = \alpha - \beta \text{ and } \varepsilon_6 = \alpha - 2\beta.$$

The six π electrons in a benzene molecule in the ground state occupy the levels ε_1, ε_2, and ε_3, so that E_{total}^{π} (benzene) $= 6\alpha + 8\beta$. This value differs by 2β from the π-electron energy $(6\alpha + 6\beta)$ of a system with three localized π bonds. Therefore, E_D (benzene) $= 2\beta$.

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* The sequence of ε's subindices corresponds to the growth of the values of ε and does not coincide with the sequence of x's subindices.

Quite often, when calculating the delocalization energies of cyclic polyene systems, the latter are compared with isoconjugated acyclic polyenes, e.g. benzene with hexatriene etc.

In the general case the following expressions for orbital energies of monocyclic polyenes can be obtained:

$$\varepsilon_\mu = \alpha + 2\beta \cos\left(\frac{2\pi\mu}{N}\right) \qquad (12)$$

$$(\mu = 1, 2, \ldots, N).$$

Substituting the indicated values of μ into Eq. (12), we get the π-orbital energies of the system.

Cyclobutadiene. For a cyclobutadiene molecule $(N = 4)$ Eq. (12) yields the following results: the molecule contains one bonding π-MO $(\varepsilon_1 = \alpha + 2\beta)$ accommodating two electrons, two nonbonding π-MOs $(\varepsilon_2 = \varepsilon_3 = \alpha)$ accommodating one electron each, and one antibonding vacant π-MO $(\varepsilon_4 = \alpha - 2\beta)$.

Thus, cyclobutadiene must be a very unstable and reactive compound, as it is indeed the case.*

Willstätter's discovery. In 1905 the German chemist R. Willstätter obtained from the pseudopelletierine alkaloid a substance to which he ascribed the following structure:

This is cyclooctatetraene. However, Willstätter was distrusted because it was considered, in accordance with the conceptions of his time, that a cyclic polyene must exhibit the "benzene-like" properties, that is, readily enter into substitution reactions and very reluctantly into addition reactions. As to the compound obtained, it behaved quite differently, not entering into substitution reactions and easily adding bromine.

Only 43 years later the veracity of the German chemist was proved. Cyclooctatetraene has no aromatic properties

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* However, the one-electron approximation is inadequate for describing the ground state of cyclobutadiene which according to more thorough calculations is likely to be singlet.

because its molecule is not planar but is shaped like a tub:

Moreover, this molecule is believed to have the ability of turning "inside out" via a transitional plane structure. At the same time it was demonstrated that in a plane cyclooctatetraene molecule the bond lengths do not get equalized, the double bonds retaining their distinctive features. Even if this molecule were plane, it would still be nonaromatic.

In Chapter 4 we shall return to the problem of finding out when a system manifests aromatic properties. Just now we shall dwell on a very important criterion of aromaticity, the Hückel rule.

The Hückel rule. First, look at Fig. 5 showing the graphic method of determining the relative arrangement of MOs which was proposed by A. A. Frost and B. Musulin in 1953. A regular N-gon is inscribed into a circle so that one of its vertices is located at the lowest point. Each of the angles of that N-gon has the corresponding π-MO shown on the right side of the figure, the nonbonding MOs ($\varepsilon = \alpha$) lying on the horizontal line passing through the centre of the circle.

It can be seen in Fig. 5 that monocyclic hydrocarbons C_nH_n have filled shells (all BMOs are occupied) if the number of their π electrons is equal to $4n + 2$, where $n = 0, 1, 2, \ldots$. This is the Hückel rule. It prescribes that the aromatic monocyclic compounds should possess 2, 6, 10 ... π electrons.

Clearly, neither cyclobutadiene nor (even plane) cyclooctatetraene can be aromatic systems since they possess $4n$ p_π-electrons.

Non-benzoid aromaticism. From the Hückel theory it follows that such systems as cyclopropenyl cation, cyclopentadienyl anion, cycloheptatrienyl cation (also called tropylium cation) and others must exhibit aromatic properties.

The discovery of the two latter ions has an interesting story. The $C_5H_5^-$ ion was discovered as early as 1901, but
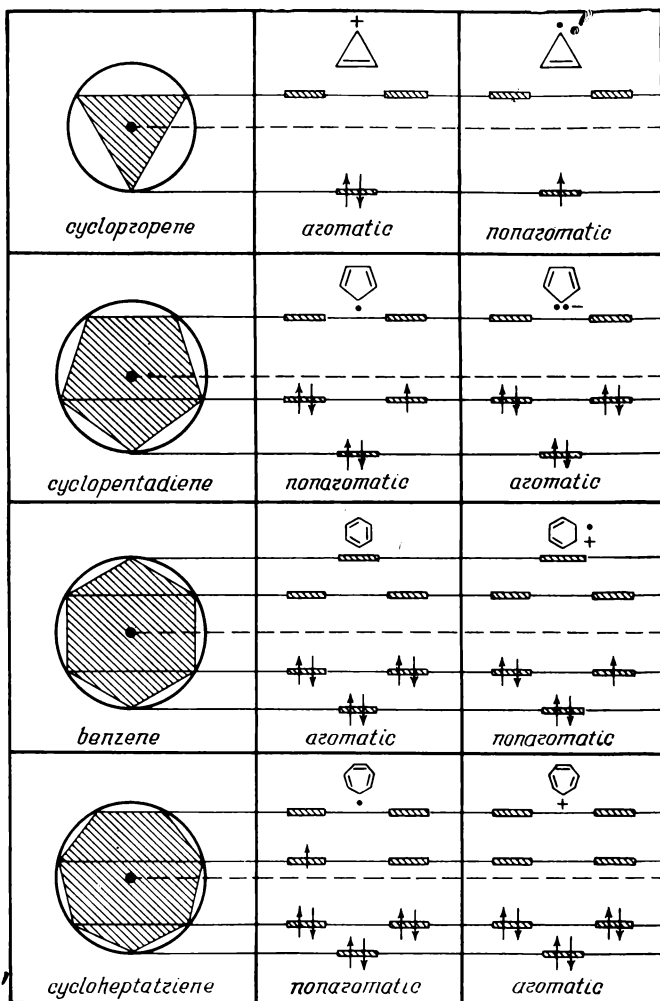
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Fig. 5

only 50 years later did it attract the attention of re-
searchers when the first "sandwich" compound, ferrocene*,

* See p. 28 in the book *Symmetry in the World of Molecules*
mentioned above,

was obtained which proved to have aromatic properties similar to those of benzene. As to the discovery of tropylium bromide by Merling in 1891, nobody noticed it at all, and Merling himself thought it to be a solid isomer of dibromocycloheptatriene. At the beginning of 1930s Hückel (not knowing, of course, about Merling's work) predicted the existence of tropylium bromide. Only in 1954 did Dering and Nocks succeed in the intentional synthesis of C_7H_7Br.

For the time being we shall drop the subject of aromatic systems and continue with the analysis of the Hückel method.

The order of a chemical bond. Many concepts of the classical theory of chemical structure were further generalized and developed in quantum theory of molecules. Here we shall touch upon one of such concepts, the bond order.

Let us leaf back a few pages and look at Eq. (1) which provides the mathematical expression of the MO method in the LCAO form. When the coefficients c_{ji} are known, the order of π bonds can be calculated. The order of the π-bond between the atoms j and k is given by the following formula:

$$p_{jk} = \sum_i^N g_i c_{ji} c_{ki}, \qquad (13)$$

where i is the number of a MO, $g_i = 0$, 1, or 2, the number of electrons in the given MO.

As an example, let us consider the molecules of ethylene and butadiene.

In the former case (see p. 21)

$$p_{12} = 2 \cdot 1/\sqrt{2} \cdot 1/\sqrt{2} = 1.$$

In the latter case

$$p_{12} = 2 \cdot 0.3717 \cdot 0.6015 + 2 \cdot 0.6015 \cdot 0.3717 = 0.894 = p_{34},$$

$$p_{23} = 2 \cdot 0.6015 \cdot 0.6015 + 2 \cdot 0.3717 \, (-0.3717) = 0.447.$$

The order of a σ-bond is assumed to be equal to unity. Therefore, for ethylene the total order is equal to

$$P_{12} = 2$$

and for butadiene

$$P_{12} = P_{34} = 1.894 \text{ and } P_{23} = 1.447.$$

π-electron density at an atom. In the same manner, knowing the AO coefficients in Eq. (1), one can calculate the π-electron density q_j and the charge Q_j at the atom j. Usually it is done by means of the formulas

$$q_j = \sum_{i=1}^{N} g_i c_{ji}^2, \tag{14}$$

$$Q_j = N - q_j, \tag{15}$$

where N is the number of π-electrons delivered to the system by the atom j.

This way we obtain for butadiene:

$$Q_1 = 1 - q_1 = 1 - (2 \cdot 0.3717^2 + 2 \cdot 0.6015^2) = 0 = Q_2.$$

The definitions (13), (14), and (15) of bond orders and charges at atoms were proposed by the British chemist and physicist C. Coulson. Different definitions of the same quantities were suggested at various times by other scientists (R. Mulliken, K. Ruedenberg, L. Pauling and others). We shall not cite or analyse any of those definitions here. It is sufficient to note that after some additional simplifying assumptions all of them reduce to Coulson's formulas.

From the quantities p_{jk} and q_j one can compose a matrix whose diagonal elements are equal to q_j and nondiagonal to p_{jk}:

$$p = \begin{pmatrix} q_1 p_{12} & \cdots & p_{1N} \\ p_{21} q_2 & \cdots & p_{2N} \\ \cdots \cdots \cdots \cdots \\ p_{N1} p_{N2} & \cdots & q_N \end{pmatrix}.$$

After Coulson this matrix is called the matrix of charges and bond orders.

Systems categorized. The electronic structure of hydrocarbons is very convenient to describe if the latter are subdivided into two classes of alternant and nonalternant systems, AS and NAS in the abbreviated form.

The systems are called alternant if their carbon atoms can be conditionally divided into two groups so that each atom of one group finds itself directly bonded only to the atoms of the other group. Essentially, atoms are subdivided as follows: in graphic formulas carbon atoms are alternately marked with asterisks. If then the marked atoms become bonded only to the unmarked ones, the system is alternant. For example:

benzene   naphthalene
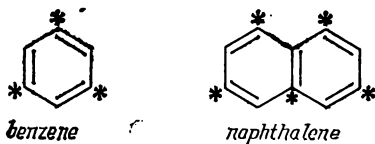
If such a marking cannot be accomplished, the system is nonalternant. For example:

fulvene   azulene
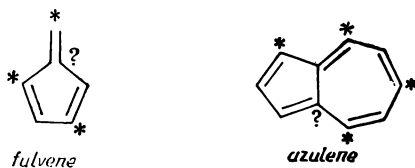
Note that alternant hydrocarbons have no odd cycles.

The classification of conjugated systems into alternant and nonalternant ones covers compounds both with even and with odd number of carbon atoms. However, certain properties of even and odd ASs may differ.

A number of remarkable theorems can be proved for ASs; the most significant of them is ...
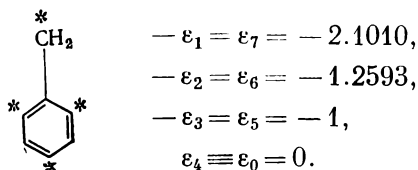
... **the pairing theorem.** Strictly speaking, that is not one theorem, but a set of them; below we shall quote a few of them.

1. Orbital energies in even ASs form pairs: $+\varepsilon_i$ and $-\varepsilon_i$.

2. In odd ASs in addition to paired levels with energies $\pm\varepsilon_i$ there is also a level with energy equal to α.

Sometimes the value α is assumed to be a zero reading, and the energy is expressed in units of β. Then it can be stated that in odd ASs there is a zero level ($\varepsilon_0 = 0$). For

example, in the benzyl radical (in units of β):

$$\overset{*}{CH_2}$$

$$-\varepsilon_1 = \varepsilon_7 = -2.1010,$$
$$-\varepsilon_2 = \varepsilon_6 = -1.2593,$$
$$-\varepsilon_3 = \varepsilon_5 = -1,$$
$$\varepsilon_4 \equiv \varepsilon_0 = 0.$$

The orbital with $\varepsilon = \varepsilon_0$ is usually called the *non-bonding* MO (NBMO).

3. If two MOs form a pair and one of these orbitals (ψ_i^+) is defined by the expression

$$\psi_i^+ = \sum_j c_{ji}^* \varphi_j^* + \sum_h c_{hi}^\circ \varphi_h^\bullet,$$

where the asterisk indicates the AOs (and their coefficients) of marked atoms and the small circle the AOs of unmarked atoms, the second MO (ψ_i^-) can be derived from the first one by changing the sign of one of the sums:

$$\psi_i^- = \sum_j c_{ji}^* \varphi_j^* - \sum_h c_{hi}^\circ \varphi_h^\bullet$$

or

$$\psi_i^- = -\sum_j c_{ji}^* \varphi_j^* + \sum_h c_{hi}^\bullet \varphi_h^\bullet.$$

4. If an AS has a single NBMO, it can be shown that the number of atoms in one group (say, the number of marked atoms) exceeds by one the number of atoms in the other group. Having marked the atoms of the larger group by an asterisk, we obtain, for the case of NBMO

$$\psi_0 = \sum_r c_{r0}^* \varphi_r^*.$$

5. The π-electron density q_i of a carbon atom in neutral ASs, both even and odd, is equal to unity.

6. In neutral ASs the order of bonds between two marked or between two unmarked atoms is equal to zero.

We have presented only a small fraction of what could be told about the structure of unsaturated organic compounds, even confining ourselves to the Hückel method. Still what has been told clearly shows how useful is this simple method of qualitative description of numerous organic molecules. During the last three decades the HMO started to be interpreted in terms of the graph theory. This aspect will be covered in the next chapter.

Topology
of Valence
Dashes

In the late fifties the Hückel method acquired a new interpretation on the basis of the graph theory. Since that time it became quite popular in chemistry, in particular, organic chemistry. Now we shall acquaint the reader with the fundamental concepts of the graph theory and its relation to the HMO method.

What Is a Graph?

Spontaneous definition. In the everyday life we come across a graph fairly often, for example, when scrutinizing the map of city streets or highways or railroads, when checking up on an electric circuit, when drawing a technological flow-sheet, and so on. Here is the most elementary definition: *a graph is a set of points connected by lines.*

The points are called the *vertices*, and the lines, the *edges* of a graph. Examples of graphs are given in Fig. 6.

The *degree* (or the valence) of a vertex is the number of edges converging at that vertex. Thus, the degree of

(a)　　　　(b)　　　　(c)
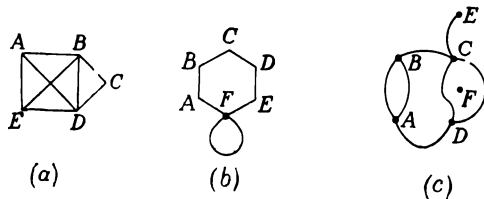
Fig. 6

vertex A (Fig. 6a) is equal to three and the degree of the vertex C in the same figure to two, etc. The vertex of degree 0 is called isolated (Fig. 6c, the vertex F), and the vertex of degree 1 is called planted or terminal (Fig. 6c, the vertex E).

When we consider a graph corresponding to a certain real object or process, or just a graph as a mathematical object, we take no interest in its metric properties, such as the shape of its edge, its length, the exact geometrical arrangement of its vertices, etc. What is important to know is *how many* vertices and *how many* edges a graph possesses and *how* its vertices are connected. If, examining two graphs G_1 and G_2, we observe that between the sets of their vertices there is a one-to-one correspondence, such that the number of edges connecting any two vertices of
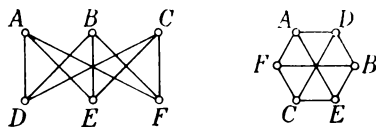
Fig. 7

G_1 equals the number of edges connecting the respective vertices of G_2, then we call the graphs *isomorphic* (see Fig. 7).

Two vertices A and B of the graph G are called *adjacent* if they are interconnected by the edge AB; in this case the vertices A and B are called *incident* at that edge and the edge AB is called *incident* at the vertices.

It may so happen that two vertices are interconnected by several edges. Then such edges are called *multiple* (Fig. 6c). An edge can connect a vertex with itself; such an edge is called a *loop* (Fig. 6b).

A graph featuring loops and multiple edges is often called a *pseudograph*, and a graph featuring multiple edges (but no loops) a *multigraph*. A graph that possesses neither loops nor multiple edges is called *simple*. Later we shall give you examples of some other kinds of graphs.

More rigorous definition. For those readers who prefer mathematical strictness we present a more accurate definition of a graph: the finite graph G is the pair $[V, E]$ comprising the following objects: (1) a finite nonvoid set V possessing p vertices and (2) a set E possessing q edges, i.e. q nonordered pairs of different vertices of V. A graph with p vertices and q edges is called a (p, q)-graph. Usually a graph is represented descriptively by a diagram which is often also called a graph.

Subgraph. Certain vertices and edges can be deleted from the graph G (Fig. 8). What is left, provided, of course, there is something left, is also a graph called a *subgraph*
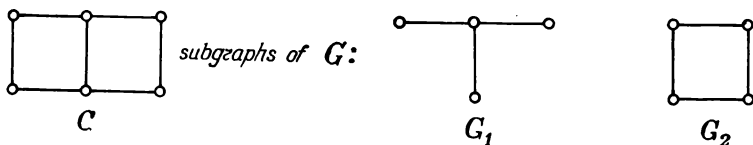

subgraphs of G:

C G_1 G_2

Fig. 8

of the graph G. Here is a more accurate definition: a subgraph of graph G is a graph whose all vertices and edges belong to G (Fig. 8).

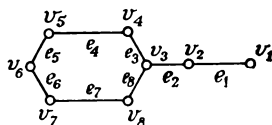**Walking around a graph.** Let us choose a graph shown in Fig. 9 as an example and take a short walk around it trav-

Fig. 9

elling along the edges from one vertex to another. The initial point of our trip will be the vertex v_1 and the final one v_8.

The alternating sequence of vertices and edges $v_1e_1v_2e_2...$ $...v_7e_7v_8$ is called a *walk*, or a (v_1, v_8)-walk. If we take some more steps and get back to the initial vertex, our walk becomes closed.

A walk is called a *trail* if all its edges are different, and a *path* if all its vertices (and edges, naturally) are different*. A closed trail is called a *cycle*. The *length of a walk* is the number of edges it contains. In our example the length of the (v_1, v_8)-walk is equal to 7. The *distance* $d(v_i, v_k)$ between the vertices v_i and v_k of the graph G is the length of the shortest path connecting these vertices.

─────────

* Only the initial and the final vertices can coincide in the case of a closed walk.

Connectivity of a graph. One of the most important properties of a graph is its *connectivity*. A graph is called connected if for any two of its vertices v_i and v_k there is a path from v_i to v_k, i.e. if we can proceed from v_i to v_k without walking twice along the same edge.

Forests and trees. The graph theory terminology is not yet fully established although the theory is about 250 years old. Frequently the terms were taken from the everyday life. For example, such words as forest, tree, knot have picked up another meaning in this theory.

To illustrate, a *forest* is a graph without cycles; if such a graph is also a connected one, it is called a *tree*. Fi-
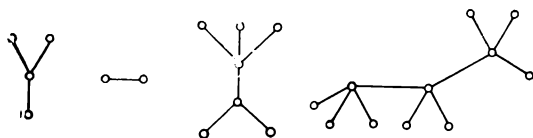
Fig. 10

gure 10 shows four trees which all together form a non-connected graph without cycles, i.e. a forest.

Molecules and graphs. For over 100 years chemists depict molecules by means of so-called structural formulas, i.e. formulas that do not specify (unless it is done deliberately) either bond lengths, or their multiplicity, or valence angles, i.e. do not indicate the metric properties of a molecule. In terms of mathematics such a formula is a graph, or a topological graph as they sometimes say, in the sense of the word used at the very beginning of the book when the topology of a molecule was discussed.

The only information that structural formulas provide is how a given atom is bonded (if at all) to others, or, in the words of Butlerov, how "the chemical interaction is distributed". Moreover, when chemists began using the graph theory, they simplified the representation of a molecule as compared to the classical one. In distinction to a structural formula a topological graph, as a rule, has no

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multiple edges. Below we give examples of topological graphs of some molecules:

H_2O $H_2C=CH-CH=CH_2$ C_6H_6
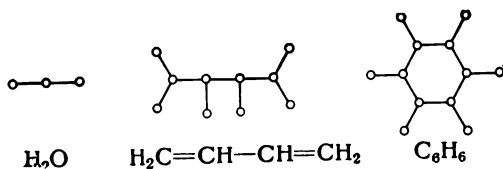
Occasionally the carbon-hydrogen bonds in organic molecules are neglected:
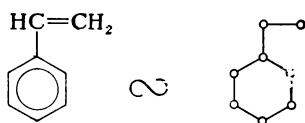
As we shall show later, many properties of molecules are defined by the shape of their topological graphs regardless of the geometry of molecules or the nature of chemical bonding in them.

Graphs, Matrices, Molecules

Thus, we have established that molecules can be represented by means of graphs. To proceed beyond this rather trivial statement, let us resort again to the mathematical graph theory and ask the following question: is it possible to represent a graph without resort to a drawing, in other words, is it possible to show the relationship of the graph's vertices not by means of points and dashes but differently, by means of other mathematical objects?

The answer is yes, and the suitable objects for the purpose are matrices.

Topological matrix of a molecule. There are several ways of establishing the correspondence between graphs and matrices. We shall dwell only on one of them, the most straightforward and convenient. When representing a molecule via a graph, we were concerned only with one aspect of its structure, namely, we wished to know whether any two atoms are chemically bonded or not. Depicting any covalent bond by an edge of a graph, we digressed from

such properties of the bond as length, strength, polarity, spatial directivity, and multiplicity.

Let us try to write a topological graph of a molecule using a matrix. To do this, we shall first of all enumerate the vertices of the graph (i.e. the atoms). Then we shall compose a certain matrix $\mathbf{A}$ with elements A_{ij}, where i and j are the numbers of the vertices (atoms).

If the atoms i and j are bonded, i.e. the vertices i and j are connected by an edge, then $A_{ij} = 1$; otherwise, $A_{ij} = 0$. The dimension of the matrix $\mathbf{A}$ is equal to the number of atoms in the molecule, N. The diagonal elements

structural formula
(hydrogen atoms omitted)

enumerated topologi-
cal graph of a molecule

$$A = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 \end{pmatrix}$$

Topological matrix of
a molecule
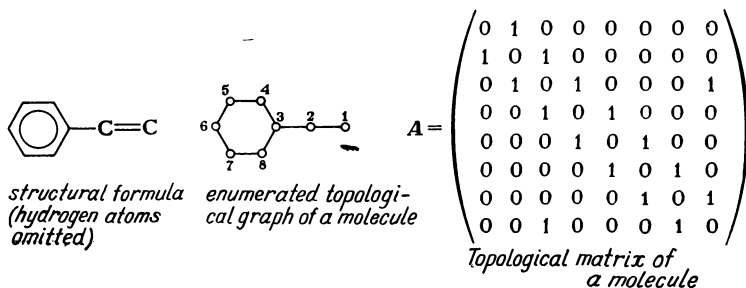
Fig. 11

$A_{ii} = 0$, i.e. a vertex is not connected with itself and the graph has no loops. Such a matrix is customarily called an *adjacency* or a *topological* matrix. As an example, a topological matrix of a styrene molecule is illustrated in Fig. 11.

From vertex to vertex. In the graph theory the matrix elements A_{ij} can be interpreted as follows: an A_{ij} is the number of unitary walks between the vertices i and j. Then the product of two elements of the matrix $\mathbf{A}$, $A_{rj}A_{js}$, is equal to 1 if the vertex r is connected with the vertex j, and the latter in its turn is connected with s, i.e. between r and s there is a walk of length 2 passing through j. If there is no such a walk, $A_{rj}A_{js} = 0$.

Let us square the matrix $\mathbf{A}$:

$$\mathbf{AA} = \mathbf{A}^2.$$

Then the element $(A^2)_{rs}$ of the matrix A^2 is equal to

$$(A^2)_{rs} = \sum_{j=1}^{N} A_{rj} A_{js}.$$

It is easy to see that the right-hand side of this equality represents the number of all walks of length 2 connecting the vertex r with the vertex s. Consequently, $(A^n)_{rs}$ is the number of all walks of length n lying between r and s.

First disappointments. Thus we have established a relationship between the graph of a molecule and its topological matrix. Unfortunately, this relationship is not unique since the appearance of the matrix A depends on the enumeration mode of the atoms in the molecule. For example, the standard enumeration of a graph with three vertices
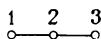
results in the topological matrix $\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$

while the enumeration
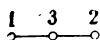
originates another matrix $\begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}$.

In search of invariants. Are there possibly any other characteristics of a graph (or its topological matrix) that are independent of the vertex enumeration mode? Yes, such invariant characteristics do exist. However, they can be obtained only after certain refinements of the theory.

Let us consider the following equality:

$$A c_i = x_i c_i \qquad (16)$$
$$(i = 1, 2, \ldots, N),$$

where c is a column matrix composed of N quantities $c_{1i}, c_{2i}, \ldots, c_{Ni}$, whose quantum-mechanical meaning will be clarified later; $(x_1, x_2, \ldots, x_i, \ldots, x_N)$ is a set

of other quantities whose physical meaning is not con-
sidered so far either.

The column matrix c_i is called an i-th *eigenvector* of
the topological matrix A, and x_i an i-th *eigenvalue* of
this matrix. The totality of eigenvalues of the matrix A
is called a *spectrum* of the graph corresponding to this
matrix.

Now let us compose the following matrix from the eigen-
vectors c_i:

$$C = (c_1 c_2 \ldots c_N).$$

Surely, the matrix C looks as a row only in the abbre-
viated notation employed above. Actually, C is a square
matrix since each of its elements C_i is a column matrix.
Using the matrix C, Eq. (16) can be written as follows:

$$AC = CX,$$

where X is the diagonal matrix

$$X = \begin{pmatrix} x_1 & & & \mathbf{0} \\ & x_2 & & \\ & & \ddots & \\ \mathbf{0} & & & x_N \end{pmatrix}$$

Bounds of the spectrum of a graph. The spectrum of
a graph possesses a remarkable property: it is *independent
of the way the vertices are enumerated*. Besides, the spectrum
has still another important property: if D_{max} is the
maximum degree of a graph's vertex, then

$$- D_{max} \leqslant x_i \leqslant + D_{max}.$$

This result is essentially the same as the theorem de-
rived by F. Frobenius in the 19th century.

The quantities x_i may or may not reach their extreme
values, but they never fall outside the interval $[-D_{max},$
$D_{max}]$.

As a rule, x_i are not integers (in contrast to D_{max}), but
some graphs have spectra consisting of whole numbers
(see Fig. 12, the values of x_i are given in braces).

In conjugated molecules $D_{max} = 3$. Therefore all
Hückel energy levels lie in the interval $[-3, +3]$. Simi-

larly, in the linear polyenes and annulenes $D_{max} = 2$ and so the extreme values of these levels are -2 and $+2$ in these molecules.
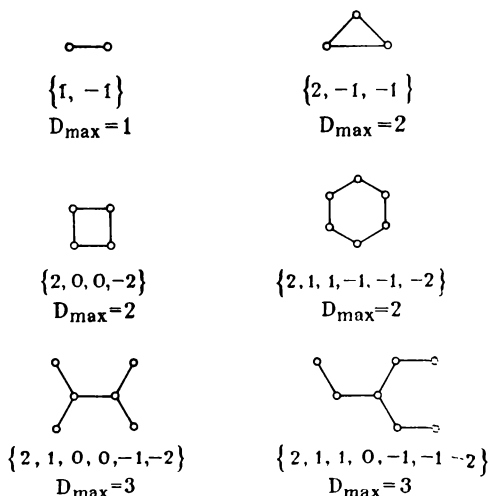

$\{1, -1\}$

$D_{max} = 1$

$\{2, -1, -1\}$

$D_{max} = 2$

$\{2, 0, 0, -2\}$

$D_{max} = 2$

$\{2, 1, 1, -1, -1, -2\}$

$D_{max} = 2$

$\{2, 1, 0, 0, -1, -2\}$

$D_{max} = 3$

$\{2, 1, 1, 0, -1, -1, -2\}$

$D_{max} = 3$

Fig. 12

Isospectral graphs. When discussing the spectrum of a graph we stressed its invariance relative to the vertex enumeration mode. Nevertheless some topologically non-equivalent graphs can sometimes possess an identical spectrum; such graphs are called *isospectral*, or, in mathematical literature, *cospectral*. The spectra of topological graphs of 1,4-divinyl benzene and 2-phenyl butadiene molecules (Fig. 13) can serve as examples.

How to determine the spectrum of a graph? Let us rewrite Eq. (16) in the form

$$(A - x_i I)c_i = 0, \qquad (17)$$

where I is a unitary matrix, and 0 is a zero matrix.

The attentive reader has guessed right: we are nearing a secular equation. Indeed, Eq. (17) has nontrivial solutions if the following condition is satisfied:

$$\det | A - x_i I | = 0. \qquad (18)$$

This secular determinant is nothing but a polynomial of x_i which is characteristic of a given graph G. This polynomial is appropriately called a *characteristic polynomial*
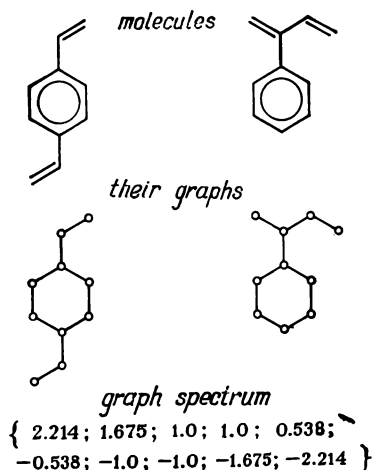

molecules

their graphs

graph spectrum

$\{$ 2.214; 1.675; 1.0; 1.0; 0.538;
$-0.538; -1.0; -1.0; -1.675; -2.214$ $\}$

Fig. 13

of the graph G and is denoted by the symbol $P_G\ (x)$:

$$P_G\ (x) = \det |\mathbf{A} - x_i \mathbf{I}| = a_0 x^N + a_1 x^{N-1} + \ldots + a_N =$$
$$= \sum_{n=0}^{N} a_n x^{N-n}. \quad (19)$$

Therefore, Eq. (18) can be replaced by the following one:

$$P_G\ (x) = \sum_{n=0}^{N} a_n x^{N-n} = 0.$$

Thus we have derived an algebraic equation of N-th degree, which has, in accordance with the fundamental theorem of algebra, N roots. However, sometimes it is not as important to calculate the roots as to analyse their properties, e.g. to find out how many positive, negative, zero roots the equation has, and so on. In such cases we have to find the coefficients of the characteristic polynomial. But how?

Sachs' theorem. In 1962-64 the German mathematician Horst Sachs (GDR) proposed an imaginative method of determining the coefficients of characteristic polynomial[*]. Here is the description of his method. Suppose a molecule can be represented by the following graph G:

Let us "expand" this graph into subgraphs whose elements are either cycles or fragments of the type o—o .

Such subgraphs are called the Sachs graphs (G^S).

In our case we can distinguish in the given graph, for example, 5 Sachs graphs shown in Fig. 14.

To proceed, it is essential to know:

(a) how many components in all the given Sachs graph $c(s)$ has and

(b) how many cyclic components $r(s)$ it features.

The numbers $c(s)$ and $r(s)$ are easy to determine. For example, for the graph G_2^S $c(s) = 2$ and $r(s) = 1$ (see Fig. 14).

$$G_1^S \qquad G_2^S \qquad G_3^S \qquad G_4^S \qquad G_5^S$$
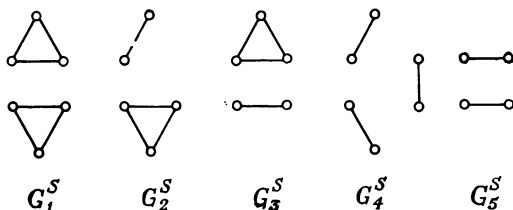
Fig. 14

Now we can formulate the **Sachs theorem:**

The coefficients of a characteristic polynomial of a certain graph G can be obtained from the following formulas:

$$a_0 = 1,$$

$$a_n = \sum_{s \in s_n} (-1)^{c(s)} \cdot 2^{r(s)} \quad (1 \leqslant n \leqslant N), \qquad (20)$$

_____

[*] The first to suggest a topological method for constructing a characteristic polynomial was C. Coulson (1950).

where S_n is the set of all Sachs graphs with n vertices and the summation is carried out over all Sachs graphs with n vertices. If S_n is a void set, then $a_n = 0$.

Let us illustrate this theorem by specific examples. We shall begin with a simple "diatomic" graph ($N = 2$) of the type

This graph is a Sachs graph and it cannot be splitted into other Sachs graphs.

Clearly, S_1 is a void set since there are no Sachs graphs with one vertex, and therefore $a_1 = 0$. Note that S_1 is always void in accordance with the definition of the Sachs graph and $a_1 = 0$ all the time.

Next, $S_2 = \left\{ \circ\!\!-\!\!\circ \right\}$, i.e. there is one Sachs graph

with two vertices; it consists of one component and has no cycles. Therefore, $c(s) = 1$, $r(s) = 0$, and $a_2 = (-1)^1 2^0 = -1$. Consequently, the characteristic polynomial takes the form (see Eqs. (19) and (20)).

$$P_G(x) = a_0 x^2 + a_1 x + a_2 = x^2 - 1.$$

Another example ($N = 4$):

This graph corresponds to the following Sachs graphs with indicated indices $c(s)$ and $r(s)$:

 $\quad c(s) = 1$, $\quad r(s) = 0$

 $\quad c(s) = 1$, $\quad r(s) = 1$

 $\quad c(s) = 2$, $\quad r(s) = 0$

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Then in accordance with the Sachs theorem:

$$a_2 = (-1)^1 2^0 + (-1)^1 2^0 + (-1)^1 2^0 + (-1)^1 2^0 = -4,$$
$$a_3 = (-1)^1 2^1 = -2,$$
$$a_4 = (-1)^2 2^0 = 1,$$
$$P_G(x) = x^4 - 4x^2 - 2x + 1.$$

Of course, the Sachs method becomes practically inconvenient for large molecules whose graphs are unwieldy, and therefore scientists proposed other methods of determining the coefficients of characteristic polynomial. Still, the Sachs method proved to be quite popular.

Corollary of the Sachs theorem. A few interesting conclusions can be deduced from the Sachs theorem. We have already obtained *corollary one:**

$$a_1 = 0.$$

Corollary two: the sum of the roots of a characteristic polynomial, that is, the sum of the eigenvalues of the topological matrix of a molecule, is equal to zero:**

$$x_1 + x_2 + \ldots + x_N = 0.$$

Corollary three: the sum of the squares of roots of a characteristic polynomial is equal to $(-2)\, a_2$:

$$x_1^2 + x_2^2 + \ldots + x_N^2 = -2a_2.$$

Corollary four: the sum of the cubes of roots of a characteristic polynomial is equal to $(-3)a_3$:

$$x_1^3 + x_2^3 + \ldots + x_N^3 = -3a_3.$$

Corollary five: the number of Sachs graphs of the type

o—o is equal to the number ν of the edges in the

initial graph G, whence it follows that $a_2 = -\nu$.

Corollary six: $a_3 = -2n_3$, where n_3 is the number of three-membered cycles in the initial graph G.

---

* In the case of compounds with heteroatoms S_1 becomes a nonvoid set and $a_1 \neq 0$.

** The sum of the eigenvalues of a matrix whose all diagonal elements are zeros is always equal to zero.

All these corollaries are not difficult to prove, and we leave the proofs for our readers. Besides, new corollaries can be derived from them, for example, these two equalities:

$$x_1^2 + x_2^2 + \ldots + x_N^2 = 2\nu,$$
$$x_1^3 + x_2^3 + \ldots + x_N^3 = 6n_3.$$

The number of corollaries can be increased for during the centuries of studies of algebraic equations mathematicians proved a great number of theorems aiding to find out the properties of their roots without solving the equations themselves, knowing only their coefficients.

But let us leave the graph theory and algebra for a while and return to chemistry. We do this to show the connection between the material discussed above and the molecular structure theory.

Two Approaches to One Problem

Topological orbitals... Probably the smartest of our readers have already appreciated the close relationship between the graph theory and the Hückel method. Actually in quantum chemistry there is a great variety of problems in which the Hamiltonian of a molecule can be written in a matrix form as a one-valued function of the topological matrix of that molecule:

$$\mathbf{H} = \mathbf{H}(\mathbf{A}).$$

In the simplest case (the Hückel method) this relation takes the form

$$\mathbf{H} = \alpha\mathbf{I} + \beta\mathbf{A}, \tag{21}$$

where α is the Coulomb integral and β is the resonance integral.

With Eq. (21) in mind, compare the Hückel equation (9) with Eq. (16) defining the spectrum of topological graph of molecule:

$$\mathbf{H}\mathbf{c}_i = \mathbf{S}\mathbf{c}_i\varepsilon_i$$

and

$$\mathbf{A}\mathbf{c}_i = \mathbf{c}_i x_i.$$

First of all it should be noted that for some types of the matrix S (see below) the eigenvectors c_i of the topological matrix of the molecule coincide precisely with those of the Hückel method, i.e. with the series of coefficients defining the molecular orbitals calculated by this method.

The coincidence of the eigenvectors of the topological matrix and Hückel's MOs follows from the fact that H and A commute, i.e. $[H, A] = 0$.

That is why the molecular orbitals calculated by the Hückel method are called *topological*.

... and their energy. But this is not enough. Let us write the overlap matrix S in the form

$$S = I + \sigma A, \qquad (22)$$

where σ is the overlap integral.

This notation corresponds to the following assumption: if the atoms are chemically connected by a "direct" covalent bonding, their orbitals overlap and the values of the overlap integrals are always equal to the same magnitude σ. If the atoms are not bonded directly, then their orbitals are supposed to be not overlapping and the respective elements of the matrix S to be equal to zero. It follows from the norming condition that the diagonal matrix elements are equal to unity. Therefore, the matrix S expressed in the form of (22) is obviously topological.

Now, substituting expression (21) for H and (22) for S into the Hückel equation (9), we obtain

$$(H - \varepsilon_i S)c_i = (\alpha I + \beta A - \varepsilon_i I - \varepsilon_i \sigma A)c_i = 0,$$

or, taking into account the properties of a unitary matrix $Ac_i = c_i x_i$ and $Ic_i = c_i I = c_i$,

$$(\alpha + \beta x_i - \varepsilon_i - \varepsilon_i \sigma x_i)c_i = 0.$$

Whence, equating the expression in parentheses to zero, we get:

$$\varepsilon_i = \frac{\alpha + \beta x_i}{1 + \sigma x_i}.$$

Thus, we have expressed the orbital energies of the simple MO method in terms of the eigenvalues of the topological matrix. If we now pass over to the simplest ver-

sion of the Hückel method, that is, apply the ZDO approximation, we have

$$\varepsilon_i = \alpha_i^{\cdot} + \beta x_i.$$

If we also recall that in this simplest version of the HMO method the value of α is often taken to be the zero reading and β a unit of energy, then

$$\varepsilon_i = x_i.$$

We have thereby clarified the meaning of eigenvalues of a topological matrix of a molecule: these values, when expressed in units of β, coincide with the orbital energies of the HMO method. In other words, *the Hückel 'method determines the MO energy values specified only by the molecular topology.*

It must be emphasized, however, that this coincidence is due to the peculiar nature of the Hückel Hamiltonian, with the short-range forces being dominant in the effective potential.

Usually the Hückel topological MOs are classified into bonding, antibonding, and nonbonding ones, depending on the sign of the respective orbital energies. The MOs corresponding to the values $x_i > 0$ are called bonding, the MOs for which $x_i < 0$ antibonding and those with $x_i = 0$ nonbonding.

The numbers of bonding, nonbonding, and antibonding orbitals are denoted by N_+, N_0, and N_- respectively, and are related to the total number N of atoms in a given graph (a conjugated molecule):

$$N_+ + N_0 + N_- = N.$$

The quantity $(N_+ - N_-)$ is called the *graph (molecular) signature*.

The graph-theoretical methods are extensively used in the theory of conjugated systems. It is only natural since in this area of chemistry the HMO method was used most frequently. In the next chapters we shall dwell on some interesting results derived in the topological theory of conjugated and aromatic systems.

Chapter Three

Graphs of Conjugated Molecules

In this chapter we shall discuss some significant results obtained in the theory of conjugated organic molecules by the graph-theoretical methods.

Coloured Graphs

How to colour a graph. In Chapter 1 we subdivided the conjugated systems into two classes, alternant and non-alternant. It is obvious that such a subdivision is based on topological features of molecules. Indeed, classifying a system as alternant, we digress from its metric properties and emphasize the way in which the atoms are interrelated. In one case the atoms are connected so that they can be categorized in the manner described on page 31, in another case their connection is quite different. How to formulate such a classification in terms of the graph theory? To do this we have to colour the graph vertices so that identically coloured vertices are not connected by any edges. It should be pointed out that in the general case the problem of colouring a graph with an arbitrary number of colours, so that the adjacent vertices are coloured differently, is extremely difficult. The solution is found, however, for some specific cases. We shall be concerned with the problem of two colours*.

The graph that can be marked in two colours is called *bipartite*, or *bichromatic*. Hereafter we shall designate the vertices of a topological molecular graph marked in one colour by an asterisk, and in another colour by a small circle, i.e. we shall keep to the designations adopted in Chapter 1. Figure 15 gives examples of bipartite (a) and

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* For all that, in principle, all chemical graphs of organic molecules can be coloured in three colours.

nonbipartite (b) graphs. The former correspond to alternant, and the latter to nonalternant systems.

Biparticity criterion. Look carefully at Fig. 15 to see that the bipartite graphs shown in it break up into the subgraphs possessing only cycles with even number of
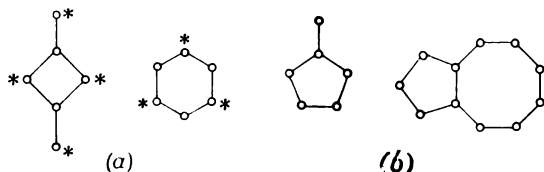

(a)   (b)

Fig. 15

vertices or not possessing cycles at all. This observation can be generalized and the following theorem proved:

The graph is bipartite if, and only if, it has no odd-membered cycles (rings) among its subgraphs.

The formal proof of this theorem was given by D. König in 1936.

Topological matrix of a bipartite graph. Bipartite graphs, just as the corresponding alternant systems, possess a number of remarkable properties. In particular, their vertices can always be enumerated so that the topological matrix is simplified and reduced to the block form

$$A = \begin{pmatrix} 0 & B \\ \tilde{B} & 0 \end{pmatrix}, \tag{23}$$

where **B** is a certain matrix which is a block of the matrix **A**, and $\tilde{B}$ is a transpose of the matrix **B**, i.e. the matrix obtained from the matrix **B** by interchanging its rows and columns: $B_{ik} \rightarrow B_{ki}$. For example, the topological matrix of a benzene molecule whose atoms are enumerated as shown (first the marked atoms are enumerated and then the remaining ones) ,
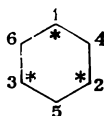
takes the form:

$$A = \begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 & 1 \\ \hline 1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 \end{pmatrix}.$$

Pairing theorem again. And how is the characteristic polynomial of a bipartite graph look like? Recalling the Sachs theorem one can easily write the expression for $P_G(x)$:

$$P_G(x) = x^N + a_2 x^{N-2} + a_4 x^{N-4} + \ldots .$$

Indeed, since a bipartite graph has no subgraphs with odd-membered cycles, the set of the Sachs graphs S_n, where n is odd, is void ($S_n = \varnothing$) and $a_n = 0$.
Therefore, when N is even,

$$P_G(-x) = P_G(x),$$

and when N is odd,

$$P_G(-x) = -P_G(x).$$

But in either case, if x_i is a root of the characteristic polynomial

$$P_G(x_i) \equiv 0,$$

then $(-x_i)$ is also its root.
On the top of that, there is at least one zero root ($x_i = 0$) for odd N (odd ASs).
Now compare the conclusions deduced to what was said in Chapter 2 and you will see that what has just been presented is nothing else but the pairing theorem formulated in terms of the graph theory.
Proceeding with our arguments, we can demonstrate that the eigenvectors of the topological matrix of a mole-

cule which correspond to the bonding MOs have the form

$$\mathbf{c}_i^{BMO} = \begin{pmatrix} c_{1i}^* \\ c_{2i}^* \\ \vdots \\ c_{pi}^* \\ \overset{\circ}{c}_{p+1i} \\ \vdots \\ \overset{\circ}{c}_{p+qi} \end{pmatrix}$$

(the vertices $1, 2, \ldots, p$ are marked, and the vertices $p + 1, \ldots, p + q = N$ are not marked).

For antibonding MOs:

$$\mathbf{c}_k^{ABMO} = \begin{pmatrix} c_{1k}^* \\ c_{2k}^* \\ \vdots \\ c_{pk}^* \\ -\overset{\circ}{c}_{p+1i} \\ \vdots \\ -\overset{\circ}{c}_{p+qi} \end{pmatrix}$$

and for nonbonding MOs (see item 4 of the pairing theorem described earlier):

$$\mathbf{c}_l^{NBMO} = \begin{pmatrix} c_{1l}^* \\ \vdots \\ c_{pl}^* \\ 0 \\ \vdots \\ 0 \end{pmatrix} = \begin{pmatrix} \mathbf{c}^* \\ 0 \end{pmatrix}. \qquad (24)$$

Thus, the complete matrix composed of AO coefficients (if NBMOs are absent) takes the following form in the case of ASs:

$$\mathbf{C} = (\mathbf{c}^{BMO};\ \mathbf{c}^{ABMO}) = \begin{pmatrix} \mathbf{U} & \mathbf{U} \\ \mathbf{V} & -\mathbf{V} \end{pmatrix},$$

where $\mathbf{U}$ and $\mathbf{V}$ are the blocks of the matrix $\mathbf{C}$.

The matrix composed of the eigenvalues of topological matrix of a bipartite graph whose vertices are properly enumerated also takes the sufficiently simple block form:

$$\mathbf{X} = \left(\begin{array}{c|c} \mathbf{Y} & 0 \\ \hline 0 & -\mathbf{Y} \end{array} \right),$$

where the matrix $\mathbf{Y} = 2\mathbf{UB\widetilde{V}} = 2\mathbf{V\widetilde{B}\widetilde{U}}$ is a diagonal matrix.

Bond orders and topology of a molecule. In 1955 the British physicist G. Hall and in 1958 the American scientists N.S. Ham and K. Ruedenberg found that the bond orders, whatever was the method of their definition (according to Coulson, Mulliken, Pauling, or otherwise), can be expressed via the topological matrix of a molecule. Thus, the matrix of bond orders and charges, constructed according to Coulson is

$$\mathbf{P} = \left(\begin{array}{cc} \mathbf{I} & 2\widetilde{\mathbf{U}}\mathbf{V} \\ 2\widetilde{\mathbf{V}}\mathbf{U} & \mathbf{I} \end{array} \right).$$

As has already been said, the system representing an even alternant hydrocarbon has a topological matrix of the type (23). Then, in accordance with the Hall theorem the matrix of orders of bonds between marked and unmarked atoms ($\mathbf{P}^{*\circ}$) is expressed by the following topological formula:

$$\mathbf{P}^{*\circ} = (\widetilde{\mathbf{B}}\mathbf{B})^{1/2}\mathbf{B}.$$

Without going into particulars over these formulas we shall formulate the general statement:

The bond order depends on the topology of a molecule, and since the bond order correlates with the bond length, the geometry of the molecule is to some extent defined by its topology.

Let Us Count Orbitals!

The foremost problem of theoretical chemistry is the stability of a chemical compound. The problem is extremely difficult because it involves two aspects, thermodynamical and kinetic. Nevertheless, in some special cases a number of rules can be established from which predic-

tions can be made. For example, stability (or instability) of some π-electron systems is often determined to a large extent by their topology.

We shall begin with the problem that is essential for chemistry, the determination of the number of bonding, antibonding, and nonbonding MOs in a certain π-electron system. From the standpoint of the graph theory the problem can be stated differently: how many positive, negative, and zero eigenvalues are there in the spectrum of the graph mapping the topology of the given π-electron system? If the number of π centres in such a molecule is equal to N (a graph with N vertices), the total number of π-MOs of all types is N. Consequently, if there are no nonbonding MOs (we shall explain later on how to establish their presence), the task becomes easier: we have to determine only the number of, say, antibonding MOs. The latter can be done by means of the graph theory, using a comparatively simple method.

Annihilate a graph! Suppose we consider a certain graph G with N vertices each of which is denoted by the letter K_i, with the index i labelling the vertices. Now let us delete one of the vertices together with the edges incident at it. This way we get a new graph that has one vertex less:

$$G_{N-1} = G_N - K_i.$$

Repeating this operation, we shall have the graph G_{N-2}. Suppose we continue deleting one vertex after another until there will be nothing left of the graph, or, as the mathematicians say, we have the void graph G_0. The sequence of graphs obtained in successive deleting of vertices from a certain initial graph, can be represented as follows:

$$\{G_N, G_{N-1}, \ldots, G_1 G_0\},$$

where $G_{N-1} = G_N - K_N$, $G_{N-2} = G_{N-1} - K_{N-1}$, etc.

This ordered set of subgraphs of a graph G is called the *expansion* of G, or the decomposition-sequence of G.

Some more designations. Making notations is an indispensable — even though boring — job and we shall occupy ourselves with it now. First, we shall denote the number of positive, zero, and negative eigenvalues in the spectrum of the graph G_n by $N_+(n)$, $N_0(n)$, and $N_-(n)$ respectively. Then, the symbol D_{N-n} will be used to denote the

determinant of a topological matrix of the graph G_{N-n} ($n = 0, 1, \ldots, N$). And finally, the sequence of numbers $\{D_N; D_{N-1}, \ldots, D_0\}$ will be designated by the symbol $[D_N]$.

Number of ABMOs. Now we can formulate the theorem on the number of ABMOs:

The number of ABMOs ($N_-(n)$) is equal to the number of sign changes in the sequence $[D_N]$.

How many ABMOs are there in pentalene? It is common knowledge that the best way to clarify the meaning of a theorem (especially this one, quoted without proof and, I regret, with some simplifications) is to give an example. As such an example, let us consider a pentalene molecule:
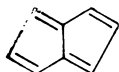
First, let us annihilate the graph of this molecule (Fig. 16) and then compose a topological matrix for each
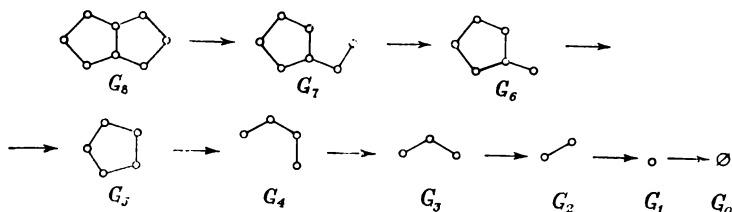
Fig. 16

of the subgraphs thus obtained and calculate its determinant. We advise the reader to do it for himself as a useful exercise*.

Here are the values of the determinants:

$$[D_N] = (0,\ -2,\ -1,\ |\ 2,\ 1,\ 0\ |\ -1,\ 0,\ |\ 1).$$

The vertical lines indicate the places in the sequence at which the sign changes. There are three such places, so $N_-(8) = 3$.

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* For a void graph $D_0 = 1$.

Some qualitative conclusions can easily be drawn from the results obtained, in particular, the tendency of the molecule to attract electrons to the NBMO. Indeed, a pentalene dianion is fairly stable.

ABMOs of benzene. Let us turn now to a benzene molecule as an example of an alternant hydrocarbon. In this case the expansion of the initial graph has the form illustrated in Fig. 17.

$$G_6 \qquad G_5 \qquad G_4 \qquad G_3 \qquad G_2 \qquad G_1 \qquad G_0$$
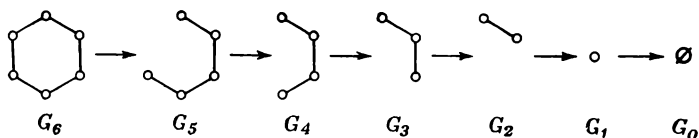
Fig. 17

Reasoning as above, we obtain the following sequence of values of the corresponding determinants:

$$[D_N] = (-4, \ 0, \ 1, \ 0, \ -1, \ 0, \ 1).$$

Whence $N_-(6) = 3$, which agrees with the results obtained above.

Thus, the described method is applicable both to ASs and to NASs.

Are there NBMOs in a molecule? In some cases the information on the stability and reactivity of a hydrocarbon can be assessed by determining whether the compound has singly populated NBMOs. In terms of the graph theory the presence of NBMOs is determined by establishing the necessary and sufficient conditions for the existence of zeros in the graph's spectrum. Below we cite a number of important theorems allowing the presence of NBMOs in a given AS to be established.

A few words on N_+. The quantity N_+, i.e. the number of bonding orbitals, can be found from the characteristic polynomial of a molecule in the following way:

$$a_N = a_{N-1} = \ldots = a_{N-N_0+1} = 0,$$
$$a_{N-N_0} \neq 0,$$
$$Ch \, (a_N, \ a_{N-1}, \ \ldots, \ a_1, \ a_0) = N_+,$$

where Ch denotes the number of changes of sign in the given sequence of coefficients. As an example, consider

fulvene$\overset{\bullet}{(}N = 6)$ (see p. 31). Its characteristic polynomial is

$$P\,(x) = x^6 - 6x^4 + 8x^2 - 2x - 1,$$

or

$$x^6 + 0 \cdot x^5 - 6 \cdot x^4 + 0 \cdot x^3 + 8x^2 - 2x - 1.$$

Then

$$Ch\,(-1,\ -2,\ +8,\ 0,\ -6,\ 0,\ +1) = N_+ \equiv 3.$$

In addition, $N_0 = 0$ and $N_- = N - N_0 - N_+ = 6 - 0 - 3 = 3$.

Six Remarkable Theorems

Theorem one — on the number of zeros. Suppose a certain alternant hydrocarbon possesses p marked and q unmarked atoms. Then the number of zeros (N_0) in the spectrum of the topological graph of this molecule obeys the inequality

$$N_0 \geqslant p - q.$$

The following corollary can be derived from this theorem: if an alternant hydrocarbon possesses N carbon atoms (N π-centres) and there are no $4m$-membered cycles, then

$$N_0 = N - 2t,$$

where t is the maximum number of double bonds that can be written in the structural formula of the given hydrocarbon.

Let us consider benzene, for example. Its molecule has no $4m$-membered cycles, $N = 6$, $t = 3$, whence $N_0 = 0$.

Generally speaking, when a conjugated⸀system possessing no $4m$-membered cycles can be expressed graphically by the Kekulé structure, i.e. the structure with alternating double and single bonds, for which $N = 2t$ all the time, the system has no NBMOs which contributes to its stability. But if this compound cannot be written in the Kekulé form, then it is a radical (*Dewar and Longuet-Higgins rule*).

Theorem two — on deletion of two vertices. If in the topological graph of an alternant hydrocarbon there is

a vertex of order one, we can delete it together with the neighbouring vertex and the edges incident at the latter without changing the number of zeros in the graph's spectrum (see Fig. 18a, b).

Theorem three — on deletion of four vertices. Briefly, this theorem can be formulated as follows: if a trail con-
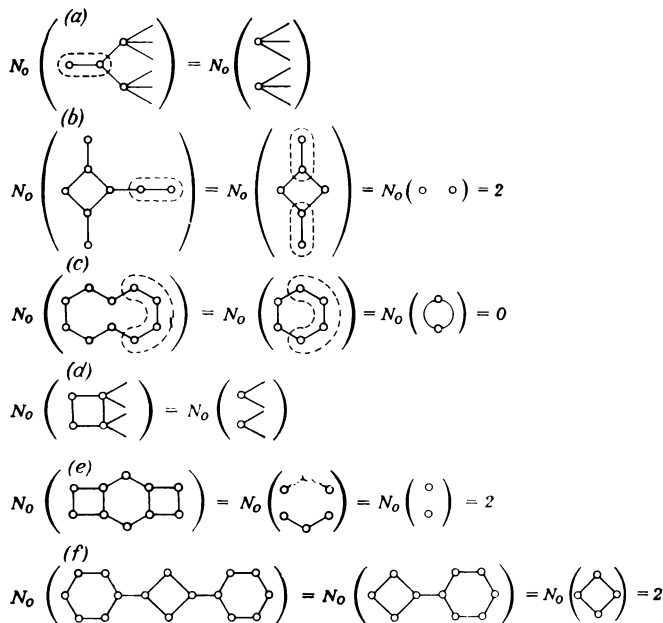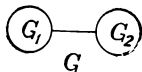

Fig. 18

sisting of four vertices is replaced by one edge, the number of zeros in the graph's spectrum remains the same (Fig. 18c).

Theorem four — on destruction of a peripheral ring. If the topological graph of an alternant hydrocarbon has a peripheral four-membered ring, two vertices and four edges can be deleted from that ring without changing the number of zeros in the graph's spectrum (Fig. 18d, e).

Theorem five — almost obvious. If the topological graph G of a molecule can be represented in the form of two sub-

graphs connected as follows:

and $N_0 (G_1) = 0$, then $N_0 (G) = N_0 (G_2)$ (Fig. 18*f*).

This seemingly trivial theorem has a practical significance: the introduction of the vinyl, phenyl, and other groups for which $N_0 = 0$ can neither *essentially* stabilize an unstable molecule, nor *essentially* destabilize a stable one.

Theorem six — on one important fragment. If the topological graph of a molecule has the fragment
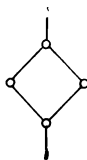
then $N_0 > 0$ (Fig. 18*f*).

More about a NBMO. Now let us get back to the vector (24) composed of the AO coefficients appearing in the expression for NBMO.

Since in the case of NBMO the values of x_i are equal to zero, for ASs we obtain from Eqs. (16), (23), and (24)

$$\tilde{B}c^* = 0. \qquad (25)$$

In an alternant hydrocarbon each unmarked atom can be connected at most to three marked ones:

$$(c_{l0}^*)\, C_l^* - C_i^\circ \diagup^{\displaystyle C_j^* \,(c_{j0}^*)}_{\diagdown\, C_h^* \,(c_{h0}^*)} .$$

The AO coefficients appearing in the expressions for the given NBMO φ_0 are given in parentheses.

Then, from Eq. (25) we get

$$c_{l0}^* + c_{j0}^* + c_{h0}^* = 0. \qquad (26)$$

As an example, let us consider the allyl radical ($CH_2 = CH - CH_2$) whose topological graph has the form

o—o—o

Let us enumerate its vertices so that the number of labelled vertices would exceed the number of unlabelled ones:

$$\overset{*}{\underset{1}{\text{o}}} - \overset{\text{o}}{\underset{3}{\text{o}}} - \overset{*}{\underset{2}{\text{o}}}$$
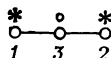
The topological matrix of this alternant system is then written in a block form as follows:

$$A = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ \hline 1 & 1 & 0 \end{pmatrix}.$$

i.e. $B = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$ and $\tilde{B} = (1\ 1)$.

The matrix of the coefficients by the marked atoms for a NBMO of the allyl radical

$$c^{HBMO} = \begin{pmatrix} c_{10}^* \\ c_{20}^* \end{pmatrix}$$

gives the following expression when multiplied by $\tilde{B}$ (see Eq. (25)):

$$(1\ 1) \begin{pmatrix} c_{10}^* \\ c_{20}^* \end{pmatrix} = c_{10}^* + c_{20}^* = 0.$$

In the general case Eq. (26) is valid for each unmarked atom of odd AS.

Eq. (26) makes it possible to find the AO coefficients of marked atoms (the remaining coefficients being equal to zero) in the expression for NBMO. Thus, for the allyl radical examined above we obtain:

$$c_{10}^* = -c_{20}^*,$$

"Redundant" Symmetry

Graph and symmetry of a molecule. The symmetry of a molecule is not manifested explicitly in its graph. For example, both graphs shown below correspond to a benzene molecule:
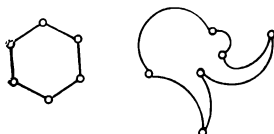
Nevertheless, we can introduce the concept of a ... ... **group of a graph.** Let us consider a noncyclic graph comprising three vertices:
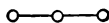
First, we enumerate the vertices of the graph. It can be done in several (more precisely, in $3! = 6$) ways, two of which are depicted below:

$$G_1 \qquad\qquad G_2$$
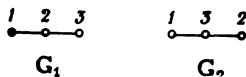
Each vertex enumeration mode corresponds to a definite permutation and its own topological matrix of the graph. Thus, graph G_1 is associated with the topological matrix

$$A_1 = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix},$$

and graph G_2 with

$$A_2 = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}.$$

The vertex permutation can be conditionally written as follows (for graph G_2):

$$P_1 = \begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix}.$$

Sometimes the upper row is omitted.
Such a notation indicates that vertex 2 in graph G_1,

whose vertex enumeration is adopted as standard, is replaced by vertex 3 in graph G_2, and vertex 3 in graph G_1 by vertex 2 in graph G_2. Vertex 1 is not involved in permutations.

The set of permutations of N vertices, or more generally, N objects, forms a group called a *permutation* or *symmetrical group* (S_N)*.

In so far as there is a group we can also speak of its representation, i.e. of a group of square matrices obeying the same group laws as the permutations themselves.

How to compose a matrix representing a given permutation? To answer this question, we shall return to our example. The permutation matrix, denoted by the symbol $\Gamma(P_1)$, is composed as follows: the matrix element located at the intersection of the second row and the third column is assumed to be equal to unity since vertex 2 is replaced by vertex 3. Accordingly, the element located at the intersection of the third row and the second column is also equal to unity for vertex 3 replaces vertex 2. After the permutation vertex 1 retains its position, and therefore the element $\Gamma_{11}(P_1)$ of the matrix $\Gamma(P_1)$ is also equal to unity. The remaining elements of that matrix are assumed to be equal to zero. Thus, the sought matrix $\Gamma(P_1)$ corresponding to the permutation P_1 has the form:

$$\Gamma(P_1) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}.$$

Similarly, the matrix

$$\Gamma(P_2) = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

corresponds to the permutation

$$P_2 = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix}.$$

---

* The readers are supposed to be acquainted with the foundations of the group theory. The most general concepts of this theory are presented in our booklet *Symmetry in the World of Molecules*, Mir Publishers, 1979. The permutation groups are well described in the excellent popular book by I. Grossman and W. Magnus *Groups and their Graphs*, Random House, 1964.

The following transformation of a topological matrix of a graph plays an important part in the graph theory:

$$A' = \tilde{\Gamma}(P)A\Gamma(P), \qquad (27)$$

where $\tilde{\Gamma}(P)$ is the transposed matrix.

For the first considered permutation of the graph's vertices the transformation (27) results in a new topological matrix differing from A:

$$A' = \tilde{\Gamma}(P_1)\, A\Gamma(P_1) =$$

$$= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix} \neq A$$

However, the same transformation performed on the matrix $\Gamma(P_2)$ leaves the topological matrix A invariant:

$$A' = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = A.$$

Thus, in the latter case the permutation of vertices P_2 leaves the topological matrix A invariant with respect to the transformation (27):

$$A = \tilde{\Gamma}(P)\, A\Gamma(P). \qquad (28)$$

The latter transformation is called the *automorphism* of a graph. The totality of all automorphisms of a graph forms a group (a group of graph's automorphisms) which is in fact a subgroup of its vertex permutation group. As we have seen already in the considered example, far from all permutations enter a group of graph's automorphisms.

More rigorous approach. Now let us formulate the obtained results more strictly. In Chapter 2 we introduced the concept of isomorphism of a graph. The isomorphic mapping of one non-oriented graph onto another is a one-to-

on mapping of vertices and edges of one graph onto the respective vertices and edges of another, so that the incidence relations are maintained. Two graphs are isomorphic if there is an isomorphic mapping of one graph onto the other (see, e.g., Fig. 7).

The automorphism of a graph is the isomorphic mapping of that graph on itself. For example:
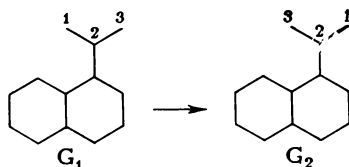
The totality of all automorphisms of a graph forms a group. This group is a group of vertex permutations and is called a vertex group of a graph, or just a group of a graph. When edges are interchanged instead of vertices, we deal with an edge group of a graph. When graphs represent molecules, both (vertex and edge) groups are isomorphic provided we do not use graphs with loops and multiple edges.

Additional symmetry. When certain organic molecules were studied by the Hückel method an interesting and significant property of their topological Hückel graphs was found: *the total group of such a graph can consist of a greater number of elements than a conventional geometrical group of symmetry.*

Let us consider, as an example, a diphenyl molecule which can be represented by the following graph:
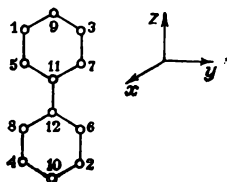
When the vertices of the given graph are enumerated as shown, its topological matrix takes the form

$$
A = \begin{pmatrix}
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 1 & 0
\end{pmatrix}
$$

The geometrical symmetry group of a topological graph of a diphenyl molecule includes four elements: the identity transformation E and three symmetry axes of second order $C_2^{(x)}$, $C_2^{(y)}$, and $C_2^{(z)}$.

We omit the plane of the drawing as a symmetry element because the reflection in this plane produces no vertex permutations, reducing thus to the element E. The four symmetry elements of the graph which were mentioned above form group D_2 and correspond to the following permutations:

$$
P(E) = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 \\ 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 \end{pmatrix},
$$

$$
P(C_2^{(z)}) = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 \\ 3 & 4 & 1 & 2 & 7 & 8 & 5 & 6 & 9 & 10 & 11 & 12 \end{pmatrix},
$$

$$
P(C_2^{(y)}) = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 \\ 4 & 3 & 2 & 1 & 8 & 7 & 6 & 5 & 10 & 9 & 12 & 11 \end{pmatrix},
$$

$$
P(C_2^{(x)}) = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 \\ 2 & 1 & 4 & 3 & 6 & 5 & 8 & 7 & 10 & 9 & 12 & 11 \end{pmatrix}.
$$

We advise the reader to construct the matrices of these permutations for themselves.

Now let us turn one (for example, lower) ring of a diphenyl molecule through the angle of 180° keeping the

other ring fixed, which corresponds to the permutation

$$P(k) = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 \\ 1 & 4 & 3 & 2 & 5 & 8 & 7 & 6 & 9 & 10 & 11 & 12 \end{pmatrix}.$$

The matrix of this permutation satisfies Eq. (28), i. e. the total group of the graph turns out to be wider than group D_2. The new symmetry element (k) of the graph together with the four others mentioned above form a group which is isomorphic to group D_{2d}. This fact is essential for understanding the features of the energy distribution of a diphenyl molecule calculated by the Hückel method. If we adopt the geometrical group D_2 of diphenyl as its group of Hückel graph and assign an irreducible representation (IR) of this group to each orbital energy level, we shall obtain the following table of orbital energies (in β units):

MO energy	IR of D_2 group	IR of D_{2d} group
$-2.278-$	B_1	B_2
$-1.891-$	A_1	A_1
$-1.317-$	B_1	B_1
$-1.000--$	$B_2,\ B_3$	E
$-0.705-$	A_1	A_1
0.000		
$+0.705-$	B_1	B_2
$+1.000--$	$B_2,\ B_3$	E
$+1.317-$	A_1	A_1
$+1.891-$	B_1	B_2
$+2.278-$	A_1	A_1

The levels B_2 and B_3 turn out to be degenerate. The origin of this degeneration is not clear if one proceeds only from group D_2. However, if one proceeds from the broadened group D_{2d} of the graph, the degeneration becomes clear: this group contains a two-dimensional IR (E), according to which certain MOs of diphenyl are transformed.

Similar results were also obtained for some other molecules. For example, the Hückel graph of a triphenylmethyl radical has a geometrical symmetry group D_3 (if, again, the reflection in the plane of the molecule is omitted), whereas its total group is isomorphic to the symmetry group of octahedron (O_h), i.e. belongs to the class of cubic groups! Initially this result was obtained by means of a computer, but later the problem of additional symmetry of a topological graph of a molecule was consid-

ered in *more general terms by V. Ya. Bespalov, research
worker of Leningrad University.

The importance of "through-space" and "through-bond" interactions. What is the cause of additional symmetry? The fact is that the Hückel method does not take into account "through-space" and "through-bond" interactions. We shall clarify this using a diphenyl molecule again as an example. Let us take into account some interactions between the atoms that are not directly related (shown by dotted lines):
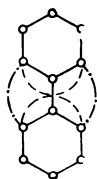
This graph will be associated with group D_2, but with different topological matrix.

We would point out once more that the presence of additional symmetry is associated with the specificity of the Hückel method, namely, with the fact that "through-space" and "through-bond" interactions are neglected. Incidentally, a similar "mysterious" degeneration (or quasidegeneration) can be observed in some other methods due to the same reasons.

Topology
of Polyene
Ribbons

In this chapter we shall resume discussing the struc-
ture of aromatic compounds. Admittedly, our narration
cannot lay claim to any comprehensive analysis of the
problem, which is feasible only in a special monograph.
Our objective is more modest. We are going to discuss the
basic aspects and difficulties of the modern theories of
aromaticity and to show to what extent the concepts of
chemical topology can be employed in investigating cy-
clic conjugated systems.

Fate of a Notion

In search of aromatic annulenes. The detailed analysis
shows that the notion of aromaticity is far from being
simple and unambiguous as it may seem at first glance.
We shall list here some complications.

When at the beginning of 1930s E. Hückel formulated
his famed $(4n + 2)$ rule, only two examples were known
which confirmed it, namely, benzene and a $C_5H_5^-$ anion.
Still, the validity of this rule is rather limited, even if
only monocyclic compounds are considered. The point is
that far from all cyclic polyenes can have a planar non-
stressed configuration. Whereas the rings of small size
with $(4n + 2)$ π-electrons are aromatic (the lengths of
the chemical bonds in such systems being equal and the
delocalization energy contributing appreciably to the
formation enthalpy), the systems with larger rings pos-
sessing $(4n + 2)$ π-electrons are no longer planar and have
no aromatic properties.

However, when carbon atoms number 14, 18, and more, a molecule becomes a planar aromatic system again. Many years of persistent research had been spent before the compounds $C_{14}H_{14}$, $C_{18}H_{18}$ and others were obtained. The authors called them [14] and'[18]annulenes respectively. [18]annulene is the first (after benzene) cyclic polyene with $(4n + 2)$ π-electrons, whose planar conformation is stable at room temperature. It is less stable than benzene, but is more stable than the corresponding acyclic polyene (nonaene):

$$CH_2=CH-(-CH=CH-)_7-CH=CH_2.$$
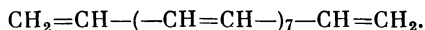
As to the [N]annulenes with $n < 18$, they are not planar due to the repulsion of hydrogen atoms located inside the ring. In the case of [14]annulene the planar conformation is stable only at $t = -60°C$.

However, hydrogen atoms are not present inside the cycles such as the one shown below:
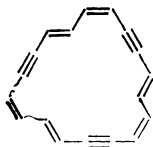
In this and similar compounds the acetylene bond is supposed to donate only two π-electrons to the conjugated system while the other π-bond is located in the plane of the molecule and does not participate in the conjugation. Consequently, this compound satisfies the Hückel rule for $n = 4$. It indeed possesses aromatic properties.

Anti-aromaticism. When a cyclic polyene system is studied it is important to know whether this system is nonaromatic, i.e.not stabilized by conjugation and sufficiently reactive due to the internal tension and other causes, or destabilized by conjugation, i.e. the cyclic delocalization increases the total energy of the system. In the latter case the molecule is called *anti-aromatic*.

Here are typical examples of anti-aromatic systems: cyclobutadiene, a cyclopropenyl anion, a cyclopentadienyl cation, and others.

As new cyclic conjugated systems were discovered the concept of aromaticity got more complicated and the

simple Hückel rule became insufficient. Some new, more general criteria of aromaticity were obviously necessary. Some of these criteria will be discussed below.

In Search of Aromaticity Criterion

Dewar's theory. In recent years more and more popular in organic chemistry becomes the theory of perturbation molecular orbitals (PMO) worked out by the American chemist M.J.S. Dewar. Using that theory, many complex problems of organic chemistry can be tackled, including the problem of aromaticity. Since it is impossible to describe this theory here, we are citing only some of the conclusions concerning the cyclic polyenes, drawn from it.

Let us consider the interaction of two odd alternant hydrocarbons R and S:

$$R + S \rightarrow RS.$$
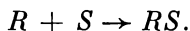
Such systems possess nonbonding MOs (Fig. 19) which on the formation of the molecule RS produce two MOs one
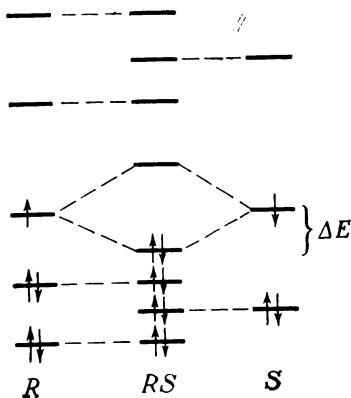
Fig. 19

of which, the lower one, is filled with two electrons. As was shown by Dewar, in the first approximation the change in the energy of the system $(R + S)$ on the formation of RS is only due to the interaction of nonbonding MOs.

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If R and S are joined by means of the atom r in R and the atom s in S
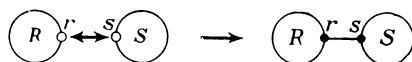
the indicated change of one-electron energy is determined by the following formula:
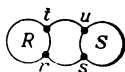
$$\Delta\varepsilon = a_{r0}b_{s0}\beta_{rs},$$

where a_{r0} and b_{s0} are the AO coefficients of the atoms r and s in the expression for a NBMO.

Then the change in the total π-electron energy will be twice as great:

$$\Delta E_\pi = 2a_{r0}b_{s0}\beta_{rs}, \tag{29}$$

since *two* electrons lost some of their orbital energy.

If the two odd ASs react at two "points" of molecule each

the change in the total π-electron energy (in this type of bonding) is equal to ΔE_π for every two interacting points of the initial molecules:

$$\Delta E_\pi = 2a_{r0}b_{s0}\beta_{rs} + 2a_{t0}b_{u0}\beta_{tu}. \tag{30}$$

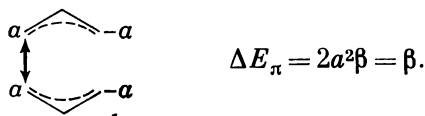Let us consider a benzene molecule as an example. We may picture benzene resulting from bonding two allyl radicals:
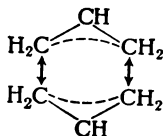
According to Eq. (26) the NBMO coefficients of an allyl radical are equal to

$$a = 1/\sqrt{2}.$$

Now we can easily obtain the value of ΔE_π which in the case of benzene equals:

$$\Delta E_\pi = 2a^2\beta + 2a^2\beta = 2\beta.$$
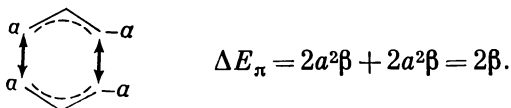
For a molecule of 1,3,5-hexatriene:

$$\Delta E_\pi = 2a^2\beta = \beta.$$

Whence it is clear that the formation of benzene is a more favourable process (in terms of energy) than the formation of hexatriene because in the former case the total energy of the system decreases by a greater value. In other words, benzene is more stable than the corresponding acyclic triene.

Dewar suggested the general method of assessing relative stability of even alternant systems. To do this, a molecule of such a system is to be mentally broken up into the methyl radical $CH_3^\cdot$ and the "residue" which is an odd AS.

Then the "methyl" coefficient in Eqs. (29) and (30) is equal to unity, and the coefficients of the "residue" can be found by the method described on p. 59. Eventually we come to the same conclusions as before: benzene is more stable than hexatriene (Fig. 20a) and consequently is aromatic while butadiene is more stable than cyclobutadiene (Fig. 20b) and consequently the latter is anti-aromatic.

Note the signs of the coefficients. We can conclude from what was said above that the higher or lower stability of a cyclic polyene as compared to an acyclic one depends on the combination of signs of the coefficients at the ends of the "demethylized" compound. If the signs are identical, the even AS is aromatic due to cyclic stabilization; if the signs are different, the system is anti-aromatic due to cyclic destabilization. Hence, the Hückel aromaticity

rule can•be easily formulated: an odd AS with identical
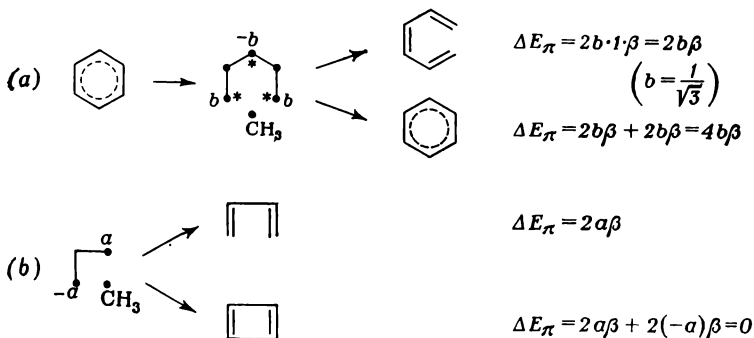signs of NBMO coefficients contains $(4n + 1)$ π-centres

(a)

$$\Delta E_\pi = 2b \cdot 1 \cdot \beta = 2b\beta$$

$$\left(b = \frac{1}{\sqrt{3}}\right)$$

$$\Delta E_\pi = 2b\beta + 2b\beta = 4b\beta$$

(b)

$$\Delta E_\pi = 2a\beta$$

$$\Delta E_\pi = 2a\beta + 2(-a)\beta = 0$$

Fig. 20

plus one π-centre at the methyl radical, i.e. the total
number of π-electrons must be $(4n + 2)$.

Polycyclic systems. Dewar has extended his method to
include the polycyclic polyenes. Fig. 21 illustrates the

decapentaenes
$\Delta E_\pi = 2d\beta$

1-phenylbutadiene

[10]-annulene
$\Delta E_\pi = 4d\beta$

azulene

$$\left(d = \frac{1}{\sqrt{5}}\right)$$
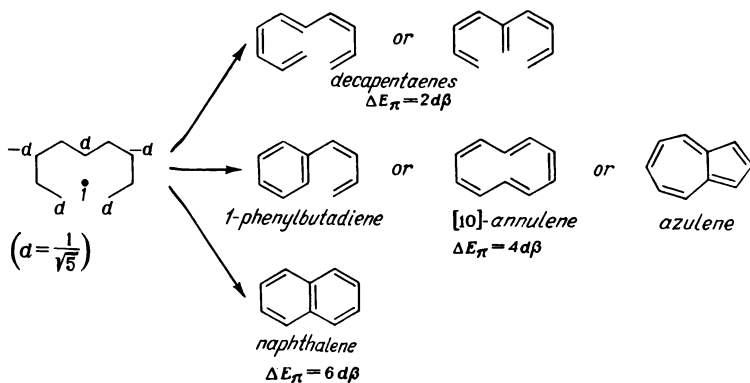
naphthalene
$\Delta E_\pi = 6d\beta$

Fig. 21

binding of methyl with nonatetraenyl resulting in the
formation of various systems, both closed and with open
chain. The highest stabilization occurs in the formation
of naphthalene which actually possesses aromatic proper-

ties, although not to the same extent as benzene. Similarly, it is easy to show that pentalene and heptalene are anti-aromatic (Fig. 22).
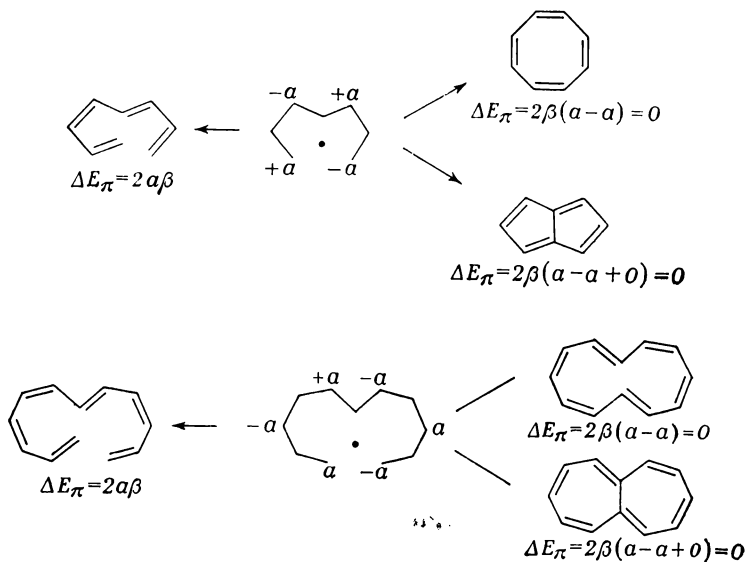

$$\Delta E_\pi = 2\,a\beta$$

$$\Delta E_\pi = 2\beta(a-a) = 0$$

$$\Delta E_\pi = 2\beta(a-a+0) = 0$$

$$\Delta E_\pi = 2a\beta$$

$$\Delta E_\pi = 2\beta(a-a) = 0$$

$$\Delta E_\pi = 2\beta(a-a+0) = 0$$

Fig. 22

Aromaticity according to Dewar. The general Dewar rule can be formulated as follows:

To determine the character of an even alternant cyclopolyene, one has to consider an odd alternant system obtained from the initial cycle by deleting one carbon atom. The binding of this odd AS to the methyl group results either in an even cyclic AS or in an even AS with one of its rings open. A cyclic system is more stable than any of the compounds with open chain, i.e. is aromatic, only when the NBMO coefficients of the respective atoms in the odd system have identical signs. Otherwise, the cycle is anti-aromatic.

The Dewar aromaticity rule just cited holds if a considered cycle possesses $(4n + 2)$ π-centres and does not if the number of π-centres equals $4n$, whence follows ...

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...Dewar-Hückel aromaticity rule. In a polycyclic alternant hydrocarbon a cycle with $(4n + 2)$ π-centres is aromatic whereas a cycle with $4n$ π-centres is anti-aromatic.

Dewar also formulated some other rules according to which various cyclopolyenes can be classified with aromatic compounds. However, we shall not dwell on them here, addressing the readers to the excellent monograph by M. J. S. Dewar and R. C. Dougherty*.

Apparently, it became clear from the previous chapters that the Dewar theory is essentially topological although it does not use explicitly the terminology and methods of the graph theory.

Modulo 4 rule. Thus, the Hückel $(4n + 2)$ rule predicts that $(4n)$ annulenes are thermodynamically much less stable than $(4n + 2)$ annulenes (e.g. compare benzene and cyclobutadiene). I. Gutman and N. Trinajstić advised to distinguish this rule from another regularity appearing also in the case of polycyclic conjugated systems, namely that the cycles containing $(4n + 2)$ π-electrons are stable while those with $4n$ π-electrons are not (e.g. compare cyclopentadienyl anion and cation).

Every cyclic conjugated structure can be characterized by its topology in terms of the ring mode. The mode of a ring can be expressed by one of the numbers from 0 to 3. Thus, a ring system of mode 0 corresponds to a $4n$ cycle $(4n \equiv 0$ modulo 4$)$, rings of mode 1 to $(4n + 1)$ systems $(4n + 1 \equiv 1$ modulo 4$)$, etc. Since the Hückel rule can be generalized to include polycyclic conjugated systems, rings of mode 2, i.e. $(4n + 2)$ systems, produce the stabilizing effect whereas rings of mode 0 produce the destabilizing effect (cf. cyclobutadiene, benzocyclobutadiene, and biphenylene). The size of a ring is also important. As n becomes sufficiently large, the difference between the rings of mode 2 and mode 0 gradually disappears.

Although rings of modes 1 and 3 do not stabilize or destabilize a molecule, their presence in the polycyclic conjugated systems manifests itself in their red-ox behaviour. Hence, the systems containing rings of mode 1 can be easily transformed into the anionic form while mole-

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* M.J.S. Dewar, R. C. Dougherty. *The PMO Theory of Organic Chemistry*. A Plenum/Rosett Ed., N. Y., 1975.

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cules containing a ring of mode 3 can be easily oxidized, that is transformed into the cationic form.

Topological π-resonance energy. The concept of the π-resonance energy, or, in other words, the delocalization energy (see p. 24), of conjugated molecules has served for many years as a simple criterion of aromaticity. The π-resonance energy (RE) in β units is defined as

$$\Delta E_\pi^{RE} = E_\pi \text{ (conjugated molecule)} -$$

$$- E_\pi \text{ (hypothetical reference structure)}$$

(see p. 18).

The main difficulty with the RE concept is the hypothetical nature of the reference structure, its choice being somewhat arbitrary. There are many ways of defining RE (M. Dewar, C. F. Wilcox, and others). Here we shall briefly examine the *topological resonance energy* (TRE). TRE is a nonparametric index which is directly related to the topology of a molecule and is of great practical value in predicting the aromatic stability of an arbitrary π-network.

The TRE can be simply expressed as follows:

$$E^{TRE} = \sum_{j=1}^{N} g_j (x_j - x_j^{ac}),$$

where N is the number of vertices (atoms) in a graph (conjugated molecule) G, g_j is the occupancy number of the j-th MO, x_j ($j = 1, 2, \ldots, N$) are the roots (eigenvalues) of the characteristic polynomial of the given graph (molecule) G, or, in other words, the individual orbital energies, and x_j^{ac} are the roots of the acyclic polynomial corresponding to this graph and called a reference polynomial:

$$P^{ac} (G; x) = \sum_{n=0}^{N} a_n^{ac} x^{N-n},$$

$$a_n^{ac} = \sum_{S \in S_n^{ac}} (-1)^{c(s)},$$

where S_n^{ac} are the acyclic Sachs graphs having exactly n vertices.

The TRE values thus obtained are used to analyse and classify arbitrary conjugated systems: the molecules with TRE (per electron) $> 10^{-2}$ are considered to be aromatic;

if $-10^{-2}_{\cdot} < TRE$ (per electron) $< 10^{-2}$ the molecules are nonaromatic; and when TRE (per electron) $< -10^{-2}$ the molecules are classified as anti-aromatic (see below).


0.046   0.039   -0.003   -0.307
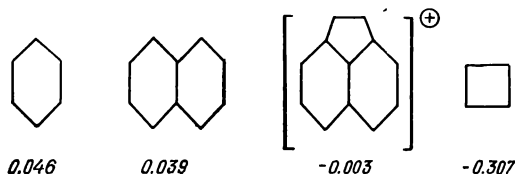
Still another (obviously topological) approach to the problem of cyclic conjugated systems are proposed in 1971 by the American scientists M. J. Goldstein and R. Hoffmann. The next section will be devoted to it.

Pseudosymmetry, Topology, Aromaticity

How to make ends meet. Let us assume that each cyclic conjugated hydrocarbon consists of several polyene ribbons connected in a certain way. Our objective is to find out how the way in which such ribbons are interconnected affects the stability of an organic molecule or ion composed of them.

For one ribbon there is the unique mode of connecting its ends:
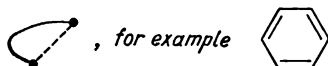
When a system comprises two polyene ribbons, the latter can be connected in two ways which are topologically nonequivalent:
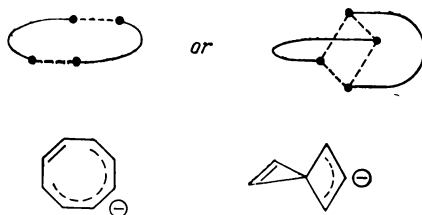

In the first case each end of one ribbon is connected only to one end of the other ribbon. Such a topology of connect-

ing the ends is called *pericyclic*. In the second case each end of one ribbon is connected to both ends of the other ribbon (the *spirocyclic* topology).
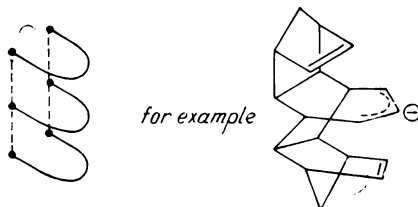
Topology of connecting three ribbons is even more diversified. Here are the most important examples: the pericyclic connection of ribbons

, *for example*
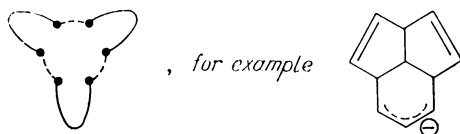
the longicyclic connection of ribbons ("keg")

for example
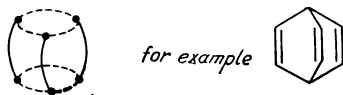
and the laticyclic connection of ribbons ("ladder")

for example

Permitted interactions of ribbons. To simplify the further discussion, let us impose some restrictions on the ribbon interaction mode. First, we assume that the ribbons interact only with their ends. Second, the ribbon twisting angle should not exceed 90°.

And ˙finally, the ends of each ribbon interact quite identically, i.e. with an equal number of other ends and via formation of bonds of the same type, either σ or π.

Pseudosymmetry of ribbon's orbitals. In our following discussion we shall be looking for symmetry of ribbon's orbitals in the case of reflection in the plane Ψ (Fig. 23).
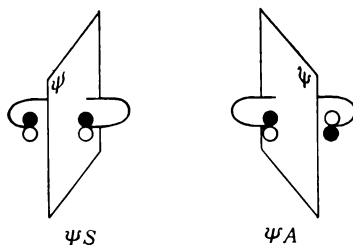

Fig. 23

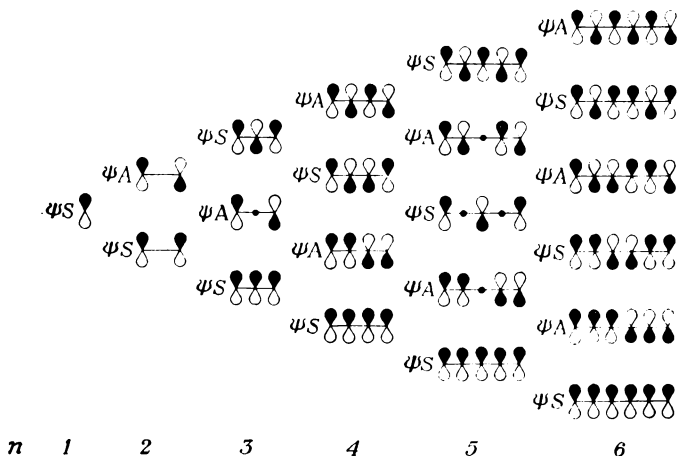Evidently, this plane is not a true symmetry plane because the specific geometrical properties of a ribbon are

Fig. 24

disregarded. In particular, the ribbon twisting is neglected as well as the presence of various substituents at its ends. Here the term "reflection in a plane" does not

imply a mirror reflection of an object. Actually we deal here with a more general problem of examining whether an object gets inverted on transition "beyond the mirror" or not. In other words, the question is whether the signs of terminal p_π-AOs of the ribbon change on reflection in the plane Ψ or not. Depending on that, we deal with pseudosymmetric (ΨS) or pseudoantisymmetric (ΨA) MOs respectively. The plane Ψ is called a *pseudosymmetry plane*.

Alternating pseudosymmetries. Looking at Fig. 24 showing the relative energy positions of MOs for the polyene series, one can easily notice that the pseudosymmetries of these MOs alternate, the lowest energy orbital being of the ΨS type.

Classification of ribbons. Now let us pass from the classification of molecular orbitals of polyene fragments to classifying the ribbons. It can be done in different ways. Sometimes it is sufficient to indicate only the number of π-electron centres (n) and the charge (z) of a polyene, denoting each ribbon by the symbol n^z. Then, for example, the fragment

will be denoted by the symbol 4^0, and the fragments
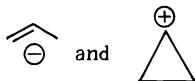
by the symbols 3^- and 1^+ respectively.

But the ribbons can be (and, for our purposes, must be) classified differently, taking into account the population density and pseudosymmetries of the highest occupied MOs (HOMO) and the lowest unoccupied MOs (LUMO). Then all polyene ribbons get subdivided into four groups (see the upper part of Fig. 25). To avoid the tiresome drawing of the MO layouts given above, we encode each layout by a certain number. Goldstein and Hoffmann advised to do it as follows: to each ribbon we ascribe the number $(n - z) \bmod 4$, where the arithmetic operation $\bmod 4$ stands for subtraction from $(n - z)$ of the maximum multiple of four, i.e. $4q$ ($q = 0, 1, 2, \ldots$)*. In other words,

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* Note that $(n - z)$ is equal to the number of π-electrons in a system.

$(n-z)\ mod\ 4$ is the remainder of division of $(n-z)$ by 4. Obviously, $4q$ must be less than or equal to $(n-z)$. Therefore, if $(n-z) < 4$, the subtrahend must be zero $(q=0)$. Thus, for example, the butadiene fragment (4^0)

LUMO ψA —	ψA —	ψS —	ψS —
HOMO ψS +—	ψS ++—	ψA +—	ψA ++—

$(n-z)\,mod\ 4:$	1	2	3	0
Examples:	2^+	2^0	2^-	2^{--}
	$3^{++},3^{--}$	3^+	3^0	3^-
	4^-	$4^{++},4^{--}$	4^+_-	4^0
	5^0	5^-	$5^{++},5^{--}$	5^+
	6^+	6^0	6^-	$6^{++},6^{--}$
	$7^{++},7^{--}$	7^+	7^0	7^-

Fig. 25

has a corresponding number $(4-0)\ mod\ 4 = 4\ (mod\ 4) = = 4-4 = 0$ and the butadienyl anion (4^-) is associated with the number $(4-(-1))\ mod\ 4 = 5\ (mod\ 4) = 1$, and so on.

It is easy to surmise that the expression $(n-z)\ mod\ 4$ takes only the values 0, 1, 2, 3, each of which can be brought into a one-to-one correspondence with one of the layouts given earlier (Fig. 25).

Acyclic connection of ribbons. Thus, we have finished the preliminary work and can set to connecting ribbons.

First, we shall connect only two ribbons and only at one location. The result will be a new acyclic polyene fragment. Let us call it intermediate. If the interacting orbitals of the initial ribbons had an identical pseudo-symmetry, e.g. ΨS, they would combine to form two MOs of the intermediate ribbon with different pseudo-symmetries, ΨS and ΨA. In this case, the energy ΨS of the intermediate MO is lower, and the energy ΨA is higher, than the energies of the initial ΨS MOs (Fig. 26a). The same is true when two ΨA MOs interact (Fig. 26b).

But if the interacting MOs have different pseudosymmetries, the energy ΨA of the intermediate MO will be lower than the initial orbital energies (Fig. 26c). Note

(a)

$\psi S + \psi S$

ψA

ψS

(b)

$\psi A + \psi A$

ψA
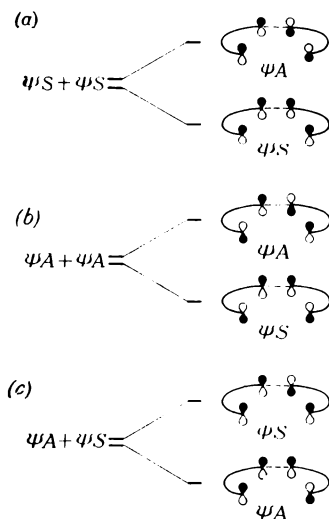
ψS

(c)

$\psi A + \psi S$

ψS

ψA

Fig. 26

that the interacting terminal orbitals of all intermediate MOs possessing higher energies are in antiphase and therefore do not overlap. That is why they are located higher than other MOs on the energy scale. For low-lying MOs the opposite is true.

A ring is completed. Let us close the cycle. In the process, the low-lying intermediate MOs must also get "closed", that is, their terminal p electron clouds must get overlapped. However, this is possible only when the MOs of the initial ribbons are of identical pseudosymmetry (Fig. 26).

Besides, on closing the cycle the energy of intermediate MOs changes in accordance with their pseudosymmetry: the energy of ΨA MO increases and that of ΨS MO decreases (Fig. 27).

We avoid using here the terms "bonding", "antibonding", and "nonbonding" MO because in the framework of the Hückel method the HOMO of a ribbon of a certain

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(e.g. 0) type may be bonding (for systems $4^0, 8^0$), nonbonding $(3^-, 7^-)$, and even antibonding $(2^{--}, 6^{--})$. Surely, the same is also true for a LUMO.

Stability of pericycles. Hereafter to simplify our presentation we shall confine ourselves to the cases where only the polyene ribbons of even types, 0 and 2, interact.
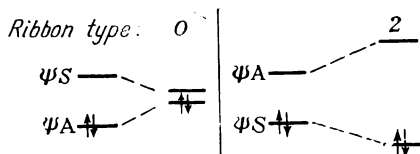

Fig. 27

Accordingly, when examining the pericycles formed by two ribbons, it is sufficient to consider the following three cases of ribbon interaction: $0 + 0$, $0 + 2$, and $2 + 2$.

Suppose the interaction is between two ribbons of type 0. Then as is seen from Fig. 28a, the pericycle formation lacks effective stabilization: two electrons increase
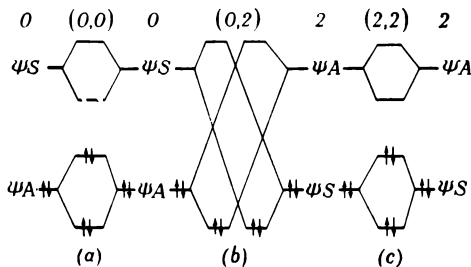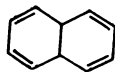

Fig. 28

their energy while two others decrease. An example of such a nonstabilized system is cis-9,10-dihydronaphthalene $(4^0 + 4^0)$ which was first obtained in 1963:

The $(2 + 2)$ interaction (Fig. 28c) is similar to that just described. As an example, we can indicate the mole-

cule of norbornadiene (bicyclo[2,2,1]-hepta-2,5-diene) relating to type $(2^0 + 2^0)$ and being a fairly reactive compound:
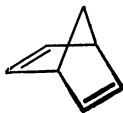
Another example is Dewar's benzene (bicyclo[2,2,0]-hexa-2,5-diene) obtained in 1963:

The latter is an unstable compound. When kept at room temperature it gradually turns into common benzene, with only about half of the initial quantity left two days later.

And only the pericyclic interaction of two ribbons of different types, i.e. the $(0 + 2)$ interaction, brings about a stabilized system (Fig. 28b). Once again we draw the reader's attention to the fact that the relative positions of MOs in Fig. 28 are shown as if only the interaction between MOs of identical pseudosymmetry existed, in accordance with what was stated earlier. Henceforth we shall be denoting the type of the obtained cyclic hydrocarbon by the symbol (k, l), where k and l are the types of the initial forming polyene ribbons.

An example of a relatively stable pericycle of type $(0, 2)$ is bicyclo[4,2,1]-nona-2,4,7-triene
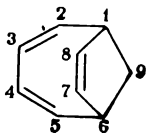
whose derivative 9-methylbicyclo[4,2,1]-nona-2,4,7-triene-9-ol was first obtained in 1963 from aromatic cyclooctatetraene dianion.

Bicyclo[4,2,1]-nona-2,4,7-triene is quite stable thermally. It sustains heating up to 450°C and only under

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ultraviolet radiation undergoes various regroupings of atoms, forming primarily tricyclononadienes.
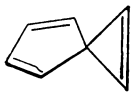
Some compounds of types (2, 2) and (0, 0) regroup comparatively easily into (0, 2) pericycles. An example is the spontaneous transformation of unstable 1,6-methanecyclodecapentaene into double norcaradiene:

(0,0) → (0.2)

The pericycle stability results obtained are summarized in Table 1.

Spirocycles. Now let us turn to the spirocyclic topology of connection of two ribbons. As in the previous case, we shall take into account only the interactions of orbitals possessing identical pseudosymmetry. The new topology, however, calls for imposing new restrictions on the ribbon

Table 1

Number of polyene ribbons	Cycle topology	Stabilized cycle type	Number of π-electrons in reach ibbon	Total number of π-electrons	Example
2	Pericyclic	(0, 2)	$4q$ $+2$	$4q+2$	Bicyclo[3,2,1]-octadienyl anion $3^- + 2^0$
2	Spirocycles	(0, 2)	$4q$ $4q+2$	$4q+2$	Spiro[2,4]-hepta-1,4,6-triene $4^0 + 2^0$

interaction modes. The interaction of two MOs of ΨS
type involves neither essential lowering nor increasing
of their energies. Therefore, when studying stable spiro-
cycles special attention should be paid to ΨA MOs.

Again, the three cases of ribbon interactions must be
considered: $0 + 0$, $0 + 2$, and $2 + 2$. Similar reasoning
enables us to come to the following conclusion: only spi-
rocycles of type (0, 2) are stable.

Unfortunately, experimental data on spirocyclic sys-
tems are insufficient so far and the number of examples
is thus restricted (Table 1).

Longicycles. As was noted before, the longicyclic
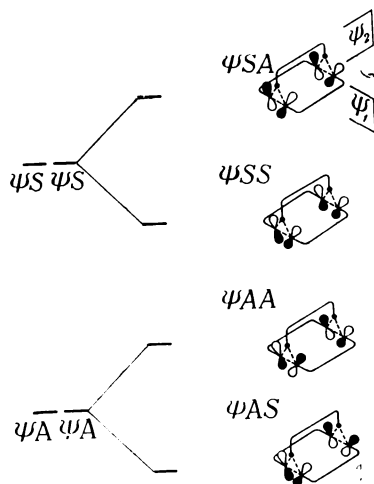topology is inherent in compounds possessing at least

Fig. 29

three polyene ribbons. Let us derive the conditions for
a stabilization of longicycle. To do this, we shall consid-
er Fig. 29 illustrating various cases of terminal-orbital
overlappings of three polyene ribbons constituting a lon-
gicycle. Let us "forget" for a while about the third (up-
per) ribbon. Then the remaining pericycle can be charac-
terized by indicating the pseudosymmetry of terminal
orbitals of constituent ribbons with respect to the planes
Ψ_1 and Ψ_2. If the orbitals of the two pericyclic ribbons are

of the type ΨAA or ΨSA, the ends of the third ribbon can effectively interact with these orbitals and all three ribbons become thus connected. In this case the third ribbon must be pseudosymmetric relative to the plane Ψ_1 if the
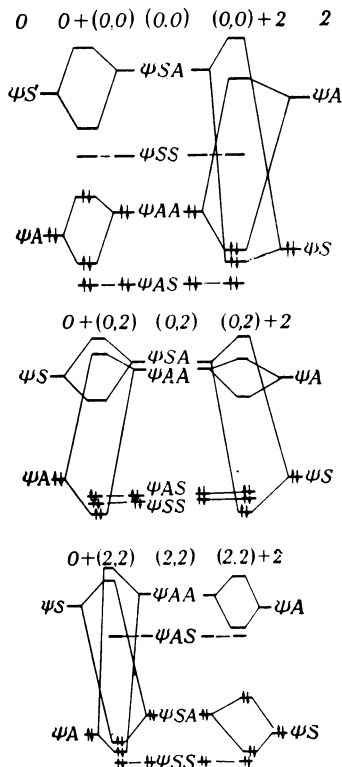

Fig. 30

two other ribbons are of the type ΨSA, and pseudoanti-symmetric relative to the same plane if the pericycle is of the type ΨAA. In other words, the effective longicyclic connection of three polyene ribbons results only in the case of the $(\Psi A + \Psi AA)$ and $(\Psi S + \Psi SA)$ interactions (see Fig. 29).

As before, we shall consider only the interaction of ribbons of the even type, i.e. we confine ourselves to the cases

$$0 + (0 + 0)$$
$$0 + (0 + 2)$$
$$0 + (2 + 2)$$

and

$$(0 + 0) + 2$$
$$(0 + 2) + 2$$
$$(2 + 2) + 2$$

The parentheses signify that we consider first the orbitals of two pericyclic ribbons and then the change of orbital energies after their interaction with the third ribbon is taken into account. The corresponding molecular orbital diagrams are shown in Fig. 30.

Studying these diagrams, one can come to the following conclusion: *stabilization is natural for the longicycles of types* (0, 2, 2) *and* (0, 0, 2)*.

The longicycles of other types, as, for example, barrelene (type (2, 2, 2))
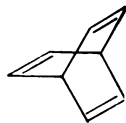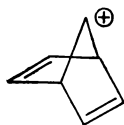

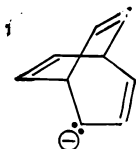and 7-norbornadienyl anion (type (2, 2, 2))
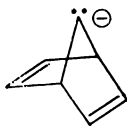
are nonstabilized.

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* Unquestionably, this conclusion is independent of the order according to which we "switch on" the ribbon interactions: $(0+2)+ 2$ or $0 + (2 + 2)$, etc.

At the, same time, 7-norbornadienyl cation of type (0, 2, 2)

is quite stable. In 1968 data were obtained on the existence of a stable anion

Laticycles. The studies of laticycles carried out by Goldstein and Hoffmann disclosed that compounds of the types (0, 0, 2), (2, 2, 0), (0, 2, 0), and (2, 0, 2) must be stable, the two last types being especially so. Unfortunately, there are no sufficiently reliable experimental data so far to confirm their conclusion.

Tips on terminology. Earlier, when characterizing one or another system, we used the adjectives "stabilized" and "nonstabilized".

It was noted in Chapter 3 that the stability of a chemical compound is a very complex concept incorporating many different aspects. Therefore, in each specific case it is necessary to explain what is meant. Here the expression "stabilized cycle" signifies that the formation of such a cycle from polyene ribbons results in lowering of the energy of corresponding π-MOs. Otherwise, the cycle is said to be destabilized. In other words, we compare the stability of a cyclic hydrocarbon to that of isolated polyene ribbons. In doing this, we look only into the π-electron energy of the system.

What was said above clearly indicates that the destabilization of the cycle must lead, as a rule, to higher reactivity of the compound. The opposite statement, however, is not generally true since even stabilized systems (in the sense indicated) can be rather reactive either due

to the presence of electric charges or due to unpaired electrons in them, or owing to some other causes.

New definitions. Thus, the stabilization of cyclic conjugated systems depends to a great extent on their topology. In fact, the hydrocarbons formed by three polyene ribbons and related to the type (2, 2, 2), i.e. possessing $4q + 2$ π-electrons, are stabilized in the case of pericyclic topology* (e.g. benzene) whereas the corresponding longicycles and laticycles are destabilized. However, in the case of "three-ribbon" hydrocarbon of the type (2, 2, 0) the opposite statement is true. Hence, it becomes possible to predict certain rearrangements proceeding along with the transformation of the system's topology, for example:

pericycle → *longicycle*
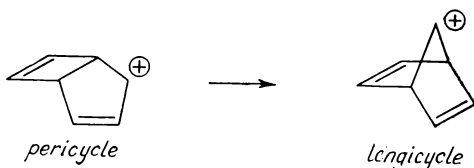
Goldstein and Hoffmann suggested the new terms: bicycloaromaticity and antibicycloaromaticity. The bicycloaromatic compounds are those cyclic conjugated hydrocarbons which contain $4q$ π-electrons and stabilized in the shape of laticycles and longicycles. The cyclic conjugated systems which possess $4q + 2$ π-electrons and are destabilized in the shapes indicated were accordingly proposed to be called antibicycloaromatic.

Future will show how useful is such a classification, but it is indisputable that the cycle topology proves to affect essentially the properties of the cycle.

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* Although earlier we did not consider the conditions for stabilization of pericycles formed from three ribbons, the result indicated can be easily derived by the reader himself.

Molecules
Without
Chemical Bonds

So far we discussed the application of the graph theory in studies of electronic structure of molecules. In this chapter we shall describe some topological concepts that appeared in stereochemistry in connection with the investigations of a new remarkable type of chemical compounds, catenanes, rotaxanes, knots.

Topological Isomerism and Topological Bonding

Let us take two wire rings which are not connected together. Nothing prevents us from arranging them arbitrarily relative to each other. Let us pass 'one of the rings through the other. Now we cannot arrange the rings arbitrarily any more.

A similar situation is observed in cyclic molecules. "Passing" one of them through another, we can obtain a new configuration in which two cycles, though nonbonded chemically, constitute a single whole. Such a bonding is called *topological*, and the composite chain molecule is called a *topological isomer* of the sum of two individual constituent molecules. The compounds of this kind are classified with catenanes (from Latin *catena*, chain) (Fig. 31*a*).

Let us consider another way of connecting molecules without chemical bond formation. If through a macrocyclic molecule passes a linear one with bulky terminal groups, the system thus obtained represents a topological isomer of the type "dumbbell in a ring" (Fig. 31*b*). Such

compounds are called rotaxanes (from Latin vords *rota*, a wheel, and *axis*).

Still another type of topological isomerism is "molecule in a cage". Formally, here belong the inclusion compounds
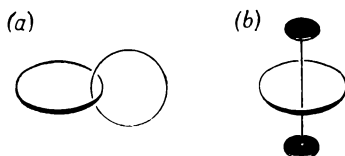
(a)   *(b)*

Fig. 31

(clathrates), carbide organometallic clusters (cryptates) (e.g. an alkali metal ion inside a macrocyclic ligand), and other systems. However, there is apparently a chemical interaction in them between a particle trapped inside the system and its surroundings.

Also known are other types of topological isomers which draw the researchers' attention, but they exist only on paper so far. Catenanes and ˙rotaxanes are the only topological structure classes which have been investigated experimentally.

Links of a Single Chain

Cycle twining. The idea of obtaining molecules consisting of two cycles passing through one another was discussed by German chemist R. Willstätter as early as the beginning of this century. However, the first efforts to synthesize catenanes failed. To pass one ring through another, it was necessary to obtain a large monocycle composed of at least 20 atoms. Such macrocycles were obtained at the middle of the 50s. In 1956-58 the problem of catenane synthesis was actively attacked simultaneously by several research teams: one headed by A. Lüttringhaus at Freiburg University, another by F. Cramer at Heidelberg, and still another by R. Kohler and B. Dietrich at Tübingen.... No success again.

Statistical synthesis. As far back as in 1952 an idea was ventured concerning an accidental formation of a catenane during the polymerization reaction, e.g. in polyphospho-

nitryl chloride. In 1960 E. Wasserman proved reliably the catenane formation for the first time. He reasoned that the cyclization of linear molecules in the presence of cyclic ones provides a chance (although a very scarce chance) for the chain to pass through the ring,
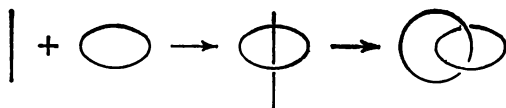

as well as for the mutual "interception" of linear molecules and the eventual formation of a catenane:

The probability of free intertwining grows with the length of molecules, but such molecules are very bothersome to work with because their solubility decreases drastically as the chain gets longer. Wasserman subjected diether $ROOC-(CH_2)_{32}-COOR$ to acyloin condensation in the presence of partially deuterated cyclotetratriacontane ($C_{34}H_{63}D_5$). The latter (not deuterated, of course) was obtained back in 1926 by the famous Swiss chemist L. Ružička during the analysis of natural aromatic musk substances.

Here is the Wasserman synthesis chart:
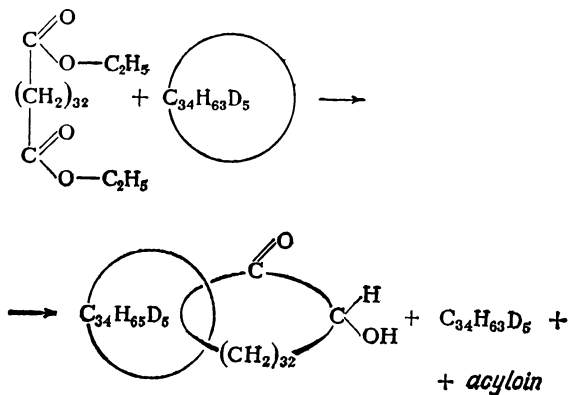
Next, the obtained mixture was separated in u chromatographic column using alumina and silica gel. In the process, $C_{34}H_{63}D_5$ was completely removed by washing the column with pentane, and acyloin was washed off by an ethermethanol solution. However, even after repeated washings the deuterated cyclic compound $C_{34}H_{63}D_5$ remained in the column. And only after the decomposition of the acyloin cycle.
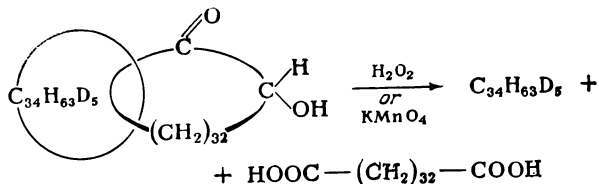
was the Ružička hydrocarbon at last drawn off the column.

These data indicated that the acyloin cycle is intertwined with $C_{34}H_{63}D_5$. Initially Wasserman recovered 5.66 mg of catenane oil, the total yield being 0.0001 per cent. Subsequently Wasserman and coworkers developed other methods of statistical synthesis of catenanes.

Directional synthesis. In April of 1964 in the laboratory of the Freiburg University G. Schill and A. Lüttringhaus succeeded in the directional synthesis of a catenane according to the following chart:
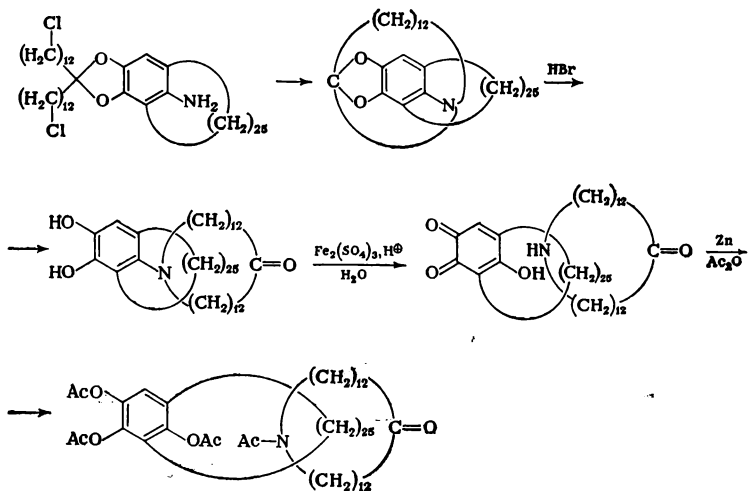
Being rather complicated (twenty stages!*), this procedure nevertheless is reliable, ensuring the correct identification of a catenane, and provides a fair 20 per cent yield.

In 1969 G. Schill and C. Zürcher synthesized a catenane consisting of three rings passing through one another:
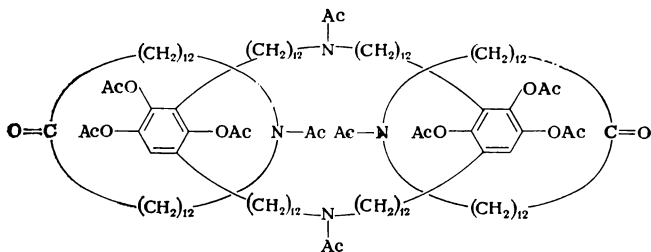
In addition to catenanes, the rotaxanes were also obtained through both statistical and directional syntheses. One of them is shown below:
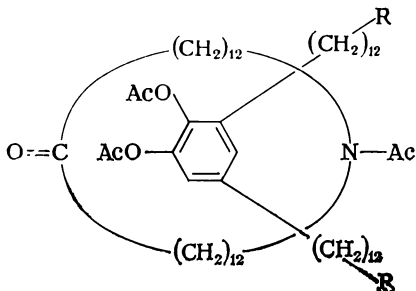
Characteristically, R have to be bulky groups.

Catenanes in nature. In 1967 the American biochemist G. Vinograd found natural catenanes. Using an electron microscope, he obtained photographs showing clearly intertwined catenanes up to a [7]-catenane. The size of individual macrocycles reached 5 µm. Later it was demonstrated that catenane DNAs are common in nature.

Syntheses of tomorrow. The search for various topological isomers in nature and the efforts of their laboratory synthesis continue. Many hypotheses and reaction charts

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* Naturally, only few stages are indicated here.

were suggested, and the properties of expected compounds predicted.

For many years chemists try to obtain twisted molecules resembling the Möbius band. The feasibility of such systems was discussed for the first time by H. Frisch and E. Wasserman as early as in 1961.

In some cycloolefin transformation reactions in the presence of transition metal compounds certain intra-
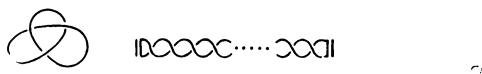

Fig. 32

molecular arrangements can be expected with the formation of knotted and twisted molecules (necktinodanes and plectanes) (Fig. 32). The synthesis of such compounds is an accomplishment of tomorrow.

Topological
Concepts
in Inorganic
Chemistry

Until now we considered the topology of various or-
ganic molecules. In inorganic chemistry the topological
methods are not so popular. Therefore, in this chapter
we shall confine ourselves to only two topics, the topolo-
gical theory of borane structure and the discussion of the
interrelationship between topology, symmetry, and ele-
ctronic structure of coordination compounds.

Boranes: Structure, Bonding, Topology

Chemistry of boron hydrides (another name, boranes) is
now one of the most challenging and rapidly growing area
of inorganic chemistry. Boranes are employed in many
fields of man's activity, primarily as missile fuels and
in cancer research.

In addition, boranes are of great interest for the chem-
ical bonding theory on which we shall dwell further.

First achievements. The founder of borane chemistry is
rightfully held to be the German chemist A. Stock al-
though the first boron and hydrogen compounds were ob-
tained back in 1881. But, according to N. V. Sidgwick,
"All statements about the hydrides of boron earlier than
1912, when A. Stock began to work upon them, are untrue".

During 25 years of persistent work Stock and his col-
leagues managed to obtain (and determine the physical
and chemical properties of) the following boron hydrides:
B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$. With the
exception of diborane, these compounds were obtained
through the interaction of magnesium boride Mg_3B_2 with

diluted acid. Diborane B_2H_6 was obtained by thermal decomposition of higher boranes. These days, as a rule, a different approach is used: first, diborane is obtained by the reaction

$$3NaBH_4 + 4BF_3 \xrightarrow{\text{in ether}} 3NaBF_4 + 2B_2H_6$$
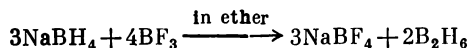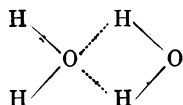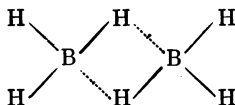
or by some other method, and then the higher boranes are produced from diborane.

Deceptive resemblance. For a long time chemists were occupied with the problem of the structure of diborane and other boron hydrides. In particular, the similarity in empirical formulas of ethane and diborane: C_2H_6 and B_2H_6 attracted attention. That is why many chemists initially accepted that diborane has an ethane-like structure. Many..., but not all. The first who had his doubts was the German chemist W. Dilthey. In 1921 at the meeting of the Erlangen Chemical Society he presented his paper "On Structure of Water" in which he suggested the following structure of dimeric water molecules $(H_2O)_2$:

$$
\begin{array}{ccc}
\text{H} & \diagdown \quad \diagup \text{H} \diagdown & \\
 & \text{O} & \text{O} \\
\text{H} & \diagup \quad \diagdown \text{H} \diagup &
\end{array}
$$

At the same time Dilthey noted that B_2H_6 can also be described by a similar model:

$$
\begin{array}{ccc}
\text{H} \diagdown & \diagup \text{H} \diagdown & \diagup \text{H} \\
 \text{B} & & \text{B} \\
\text{H} \diagup & \diagdown \text{H} \diagup & \diagdown \text{H}
\end{array}
$$

However, Dilthey's hypothesis was soon forgotten, and the idea of similarity with ethane prevailed. Only in the 40s the arguments concerning the diborane structure renewed.

As early as 1940 the American chemist F. Stitt demonstrated that in B_2H_6 the barrier hindering the internal rotation about the hypothetical B—B bond is much higher as compared to ethane. Then some more experimental data appeared to promote the hydrogen bridge structure. Dilthey's model was again taken up in the publications by B. V. Nekrasov, Ya. K. Syrkin, M. E. Dyatkina in the USSR, and some foreign chemists.

The final proof of the presence of hydrogen bridges in boranes was provided in 1948 for decaborane $B_{10}H_{14}$ and in 1951 for B_5H_9 and B_2H_6.

The theoretical description of similar structures in terms of a three-centre bonding conception (see below) was first suggested in 1943-47 by H. C. Longuet-Higgins and R. S. Mulliken. A great contribution to the investigation of structure and properties of boranes was provided by the American chemist W. N. Lipscomb who was awarded the Nobel Prize for his efforts in 1976.
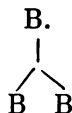
Deficiency without deficiency. Let us turn now to the electronic structure of boranes. Usually they are classified with electron-deficient compounds because the number of possible two-centre interactions exceeds the number of valence-electron pairs.

In a molecule B_2H_6 each boron atom forms two common (two-centre two-electron) covalent bonds with terminal hydrogen atoms. As to the bridge bonds B—H—B they are considered as triangular fragments in which the formation of three MOs involves one valence orbital of each atom (Fig. 33a). Each fragment contains two electrons occupying the bonding MO Ψ_1. That is how a very strong two-electron three-centre bond BHB appears which is stronger than the conventional bond B—H. Thus, there is actually no deficiency of electrons. That deficiency existed only in the earlier conceptions of chemical bonding which was always pictured as a result of two-electron two-centre interactions.

In higher boranes, in addition to the bridges BHB, there are also two types of fragments with three-centre bonds: the "open" bridge $\underset{B\quad B}{\overset{B}{\diagup\diagdown}}$ and the "closed", or "central", structure $\underset{B\quad B}{\overset{\overset{\textstyle B}{|}}{\diagup\diagdown}}$.

The molecular orbital charts corresponding to these fragments are illustrated in Fig. 33b and c.

Lipscomb's topological theorem. In 1954 W. Lipscomb with coworkers suggested a so-called topological theory of boranes which he continues to improve even now. On the basis of that theory it became possible to predict,
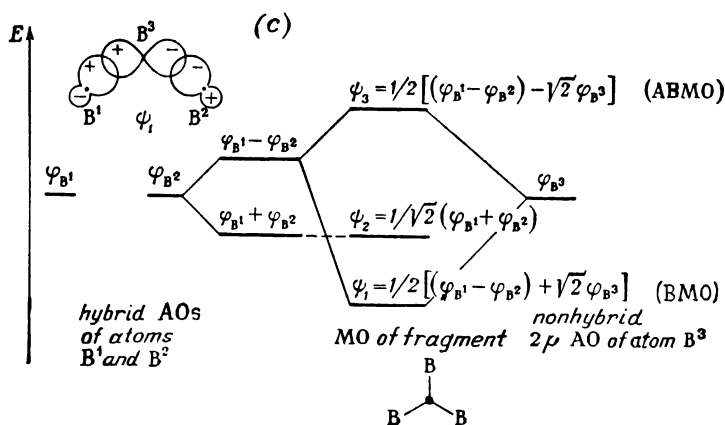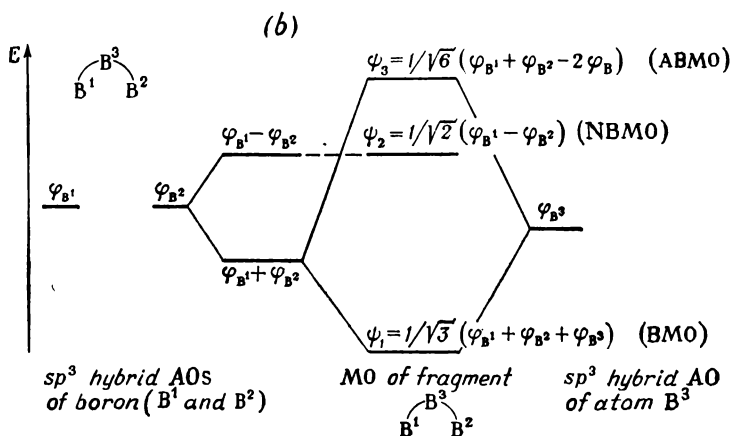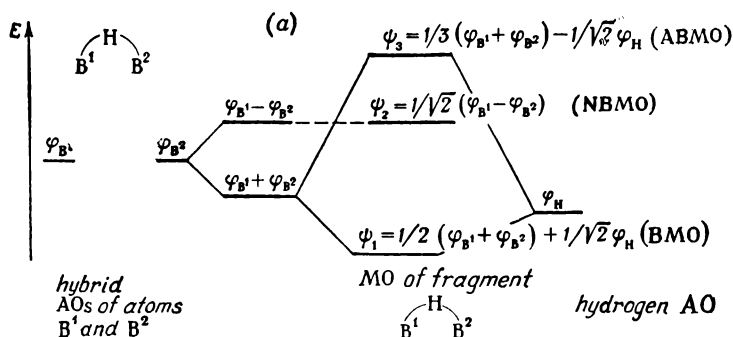
E

(a)

$\psi_3 = 1/3\,(\varphi_{B^1} + \varphi_{B^2}) - 1/\sqrt{2}\,\varphi_H$ (ABMO)

$\varphi_{B^1} - \varphi_{B^2}$ $\psi_2 = 1/\sqrt{2}\,(\varphi_{B^1} - \varphi_{B^2})$ (NBMO)

φ_{B^1} φ_{B^2}

$\varphi_{B^1} + \varphi_{B^2}$

φ_H

$\psi_1 = 1/2\,(\varphi_{B^1} + \varphi_{B^2}) + 1/\sqrt{2}\,\varphi_H$ (BMO)

*hybrid
AOs of atoms
B^1 and B^2*

MO *of fragment*

hydrogen AO

(b)

E

$\psi_3 = 1/\sqrt{6}\,(\varphi_{B^1} + \varphi_{B^2} - 2\varphi_B)$ (ABMO)

$\varphi_{B^1} - \varphi_{B^2}$ $\psi_2 = 1/\sqrt{2}\,(\varphi_{B^1} - \varphi_{B^2})$ (NBMO)

φ_{B^1} φ_{B^2}

$\varphi_{B^1} + \varphi_{B^2}$

φ_{B^3}

$\psi_1 = 1/\sqrt{3}\,(\varphi_{B^1} + \varphi_{B^2} + \varphi_{B^3})$ (BMO)

sp^3 *hybrid* AOs
of boron (B^1 *and* B^2)

MO *of fragment*

sp^3 *hybrid* AO
of atom B^3

(c)

E

$\psi_3 = 1/2\,[(\varphi_{B^1} - \varphi_{B^2}) - \sqrt{2}\,\varphi_{B^3}]$ (ABMO)

$\varphi_{B^1} - \varphi_{B^2}$

φ_{B^1} φ_{B^2}

$\varphi_{B^1} + \varphi_{B^2}$

φ_{B^3}

$\psi_2 = 1/\sqrt{2}\,(\varphi_{B^1} + \varphi_{B^2})$

$\psi_1 = 1/2\,[(\varphi_{B^1} - \varphi_{B^2}) + \sqrt{2}\,\varphi_{B^3}]$ (BMO)

hybrid AOs
of atoms
B^1 *and* B^2

nonhybrid
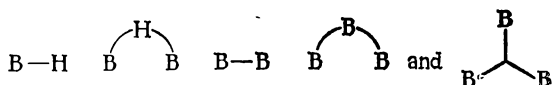MO *of fragment* $2p$ AO *of atom* B^3

Fig. 33

and then to synthesize, some boranes and their derivatives (B_7H_{15}, B_9H_{15}, $B_{11}H_{17}$ etc.). Lipscomb's topological theory is based on the balance equations derived by him and relating the borane composition with the number of certain structural elements in borane. Lipscomb distinguishes the following basic structural units:

As an example, let us consider neutral boranes with composition B_pH_{p+q}. Suppose the number of hydrogen bridge atoms is denoted by s, the number of terminal BH or BH_2 groups by x, the number of three-centre bonds BBB (both open and central) by t, and the number of two-centre bonds B—B by y.
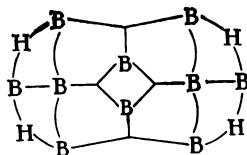
Then for hydrogen atoms the balance equation takes the form*:

$$s + x = q. \qquad (31)$$

Since each boron atom has four orbitals accommodating three electrons, the total number of three-centre bonds (BHB and BBB) is equal to the number of boron atoms in the molecule:

$$s + t = p. \qquad (32)$$

An example is a decaborane-(14) molecule whose topological graph has the form:

In this case $s = 4$, $t = 6$, and $p = 10$, and Eq. (32) is thus satisfied.

And finally, the last balance equation

$$t + y + q/2 = p \qquad (33)$$

means that each boron atom in the structures in question is connected at least to one terminal hydrogen atom. As an

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* Make sure this equation holds, e.g. in the case of diborane.

example, the reader is advised to consider the graph of decaborane-(14) shown above ($t = 6$, $y = 2$).

For borane ions with the charge c ($B_p H^c_{p+q+c}$) the balance equations take the form:

$$s + x = q + c,$$
$$s + t = p + c, \qquad\qquad (34)$$
$$t + y = p - c - \frac{q}{2}.$$

The application of these equations can be illustrated for the case of the dianion $B_{10}H^{2-}_{14}$. According to our notation, it should be written as $B_{10}H^{2-}_{10+6-2}$. This ion is represented by the following topological graph
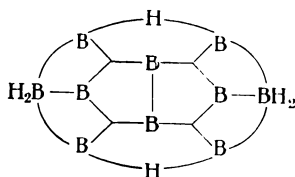
for which $s = 2$, $t = 6$, $y = 3$, $x = 2$, $c = -2$, $p = 10$, $q = 6$.

From the Lipscomb theory one can get the topological graphs for any borane of assigned composition and thus predict new structures. Certain limitations should be imposed, though, on the quantities appearing in the balance equations (31)-(34), for example,

$$q/2 \leqslant s \leqslant p \text{ (or } q).$$

Besides, one can take into account the limitations due to the symmetry and metric characteristics of compounds (e. g. the limiting values of valence angles etc.)*. So, for borane $B_{10}H_{14}$ ($p = 10$, $q = 4$) the following sets of the variables s, t, y, x ($2 \leqslant s \leqslant 4$) are possible:

s	t	y	x
4	6	2	0
3	7	1	1
2	8	0	2

---

* For example, the neighbouring boron atoms cannot be simultaneously connected by central and bridge three-centre bonds BBB since in that case the valence angles would become very small.

Thus, the topology corresponding to the set of indices $styx = 4620$ is not the only possibility for a borane of composition $B_{10}H_{14}$. The problem of the existence of a specific structure can be solved both experimentally and theoretically, by the MO method.

Weakness of the theory. Lipscomb's theory based on the assumption of localized three-centre bonds becomes inadequate as the number of hydrogen and boron atoms in molecules grows, increasing dramatically the number of possible resonance structures that should be taken into account when composing the total wave function of the molecule. Inevitably, the number of possible topological types of the molecule also grows with the increase in p and q.

It does not imply, however, that the topological theory has lost its significance to become second to the MO method. It would be more appropriate to say that the molecular orbital and topological approaches are mutually complementary. That it is really so can be seen from one of the recent papers by Lipscomb and his coworkers which is devoted to the study of unstable boranes B_2H_4, B_3H_7, B_3H_9, B_4H_8, and B_4H_{12}.

New refinements. Using the MO method to calculate the optimal geometry of these compounds, it was established that the molecules B_2H_4, B_3H_9, and B_4H_8 have vacant orbitals at a boron atom. To describe the unstable boranes with vacant orbitals, the known topological rules (the balance equations) had to be extended. The new equations for the systems B_pH_{p+q} take the form

$$s + x = q,$$
$$s + t = p - v,$$
$$t + y = p - \frac{q}{2},$$

where v is the number of vacant orbitals.

The transformation energy values of the boranes in question calculated by the MO method and by the semi-empirical equation proposed by the authors

$$E = -45v + 17\Delta s + 28\Delta t$$

agreed to within 21 kJ/mol.

This result emphasizes once more that it pays to combine rationally simple methods of treating chemical compounds and complex quantum-mechanical calculations.

Symmetry and Topology of Complexes

Now let us turn to another aspect of graph-theoretical methods used in inorganic chemistry. We shall deal with the determination, even though approximate, of the sequence of values of molecular-orbital energies in complex compounds. From the very beginning we should note that everything to be discussed can be attributed also to organic molecules possessing sufficiently high symmetry and comprising an adequate number of atoms at topologically equivalent positions. However, at present the approach described here is applied almost exclusively to high-symmetry inorganic compounds.

Topology of interligand interactions. Consider, for example, a tetrahedral molecule AL_4, where A is the central atom and L are identical σ-ligands. The topological matrix of such a molecule can be written in the form

$$A = \begin{pmatrix} k & 1 & 1 & 1 & 1 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{pmatrix}, \tag{35}$$

where k is a certain parameter characterizing the difference of the atom A from the ligands. Then the problem of determining orbital energies by the Hückel method (since we treat our complex in terms of that method) reduces in the orthogonal basis $(S = I)$ to finding the eigenvalues of the topological matrix A. For small k we obtain:

$$x_{1, 2, 3} = 0,$$
$$x_{4, 5} = 1/2k \pm 2.$$

However, some scientists believe that the matrix (35) has an essential drawback: topologically, it possesses redundant information, describing the topology of the molecule and, through the parameter k, the difference in the na-

ture of the central atom and the ligands. This drawback can be done away with in various ways. Thus, it was proposed to split the topological graph of the system AL_4 into two subgraphs (Fig. 34) and then to examine the topological matrix of the subgraph G_2. This procedure is equivalent to regarding only interligand interactions.
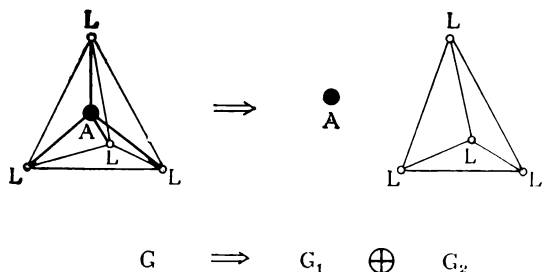

$$G \implies G_1 \oplus G_2$$

Fig. 34

Accordingly, the order of increase of orbital energies obtained thereby is defined only by the ligand-ligand interactions. As to the interactions of the ligands with the central atom (exceeding in magnitude the interligand ones!) and the modifications in molecular-orbital charts, appearing when these interactions are taken into account, they can be calculated by the methods of quantum-mechanical perturbation theory. Although this approach contradicts the adopted ideas of the relative intensity of ligand-ligand and ligand-central atom interactions, it turns out to be quite satisfactory for qualitative analysis of electronic structure of complexes.

Sequence of orbitals. The topological matrix of the graph G_2 has the form:

$$A\ (G_2) = \begin{pmatrix} 0 & 1 & 1 & 1 \\ 1 & 0 & 1 & 1 \\ 1 & 1 & 0 & 1 \\ 1 & 1 & 1 & 0 \end{pmatrix}.$$

To find the eigenvalues of this matrix, one has to solve the secular equation

$$\det |\ A\ (G_2)\ - x\mathbf{I}\ | = 0$$

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or

$$\det |\mathbf{A}(G_2) - x\mathbf{I}| = \det \begin{vmatrix} -x & 1 & 1 & 1 \\ 1 & -x & 1 & 1 \\ 1 & 1 & -x & 1 \\ 1 & 1 & 1 & -x \end{vmatrix} =$$

$$= x^4 - 6x^2 - 8x - 3 = (x+1)^2 (x^2 - 2x - 3) = 0.$$
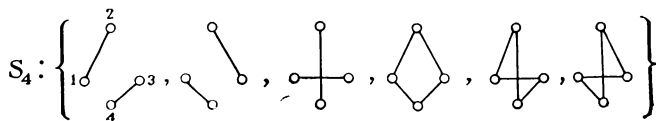
Whence

$$x_1 = +3,$$
$$x_{2,3,4} = -1.$$

Thus, three roots have the same magnitude (the triple degeneration), and all the roots are real because the matrix $\mathbf{A}(G_2)$ is Hermitian, i.e. includes only real elements and $\tilde{\mathbf{A}}(G_2) = \mathbf{A}(G_2)$.

To find the eigenvalues of the matrix $\mathbf{A}(G_2)$ we could also use the Sachs theorem:

$$P(G_2) = a_0 x^4 + a_1 x^3 + a_2 x^2 + a_3 x + a_4 = 0$$

$a_0 = 1$; $S_1 = \varnothing$; $a_1 = 0$; $a_2 = -6$ (according to Corollary 5 from the Sachs theorem, see p. 45); $a_3 = -8$ (according to Corollary 6 from the Sachs theorem, see p. 45).

$$a_4 = 3(-1)^2 2^0 + 3(-1)^1 2^1 = -3.$$

Hence:

$$P(G_2) = x^4 - 6x^2 - 8x - 3.$$

Now let us take account of symmetry. The MOs of a tetrahedral molecule are transformed according to irreducible representations (IR) A_1 and T_2 of the group T_d.

(For the sake of simplicity we assume that each ligand is represented by only one orbital of s type.) Then in a system consisting of four σ-ligands there will be one nondegenerated energy level with IR A_1 and $x_1 = 3$, and one triply degenerated level with $x_{2,\,3,\,4} = -1$ and IR T_2:

$$- - - t_2\,(x_{2,\,3,\,4} = -1),$$
$$- a_1\,(x_1 = +3).$$

Thus, knowing the topology and symmetry of a system, one can determine the most probable ordering of molecular-orbital energy levels and the degeneration structure of the energy spectrum.

Topologically equivalent groups. How is the symmetry of a compound related to its topology? Earlier we noted that the geometry (symmetry) of molecules may differ even when the topology is the same. This statement, however, has to be made more precise. To some extent topological matrices convey the symmetry of molecules because the matrix $\mathbf{A}$, as a rule, commutes with the matrices of those ligand permutations that correspond to operations of the symmetry point group (R) of the molecule*. Consider, for example, a V-shaped molecule of symmetry C_{2v} (say, a water molecule) whose topological matrix has the form

$$\mathbf{A} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

Each symmetry operation of the group C_{2v} (the symmetry group C_2 for a graph) is associated with a certain permutation of vertices in the topological graph of the molecule (Table 2).

The matrices of these permutations

$$\mathbf{\Gamma}\,(P_{13}) = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \quad \text{and} \quad \mathbf{\Gamma}\,(I) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

commute with the matrix $\mathbf{A}$ which the reader himself can easily demonstrate.

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* The matrices $\mathbf{A}$ and $\mathbf{B}$ are called commutating if the following relation holds $[\mathbf{AB}] \equiv \mathbf{AB} - \mathbf{BA} = 0$, i.e. their product is independent of the sequence of cofactors.

• *Table 2*

Permutation of graph vertices	$I = \begin{pmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \end{pmatrix}$	$P_{13} = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix}$
Symmetry operation of group C_2	E	C_2

The matrices of permutations corresponding to opera-
tions of molecular symmetry groups also form a group. Let
us denote it by P_n. The groups P_n and R are isomorphic.
In our example the group C_2 is isomorphic to the group P_2.
Since the topological matrix A commutes with the permu-
tations of the group P_n, it will also commute with the
matrices of transformations of the molecular symmetry
group. The same group P_n will correspond to isomorphic
symmetry groups. Let us use here the concept of topological-
ly equivalent groups introduced in 1968 by the German
chemist H. H. Schmidtke. If two symmetry groups are
isomorphic and the geometric bodies corresponding to
them can be obtained from one another through continu-
ous deformation, such groups are, according to Schmidtke,
topologically equivalent. If no distinction is made be-
tween topologically equivalent groups, the topology and
symmetry of a molecular graph become related in a one-
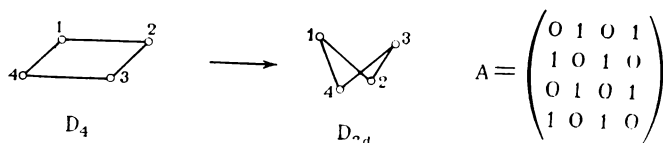to-one manner. Thus, for example, the molecules shown

$$A = \begin{pmatrix} 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \end{pmatrix}$$

Fig. 35

in Fig. 35 correspond to the topologically equivalent
groups D_4 and D_{2d}. The topologically equivalent groups
possess similar (as to the number, sequence, and degen-
eration structure) spectra of molecular-orbital energies
(Table 3).

Structural matrix. Strictly speaking, the foregoing argu-
ments are correct only if each atom provides one orbital to
form a chemical bond. When this condition is not satisfied

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the matrix A, as was shown by Schmidtke, should be replaced by a matrix of higher dimension which he called a structural matrix. Then the group P_n will represent

Eigenvalues of topological matrix A	Irreducible representations of groups	
	D_4	D_{2d}
$x_1 = +2$	A_1	A_1
$x_{2,3} = 0$ $x_4 = -2$	E B_1	E B_2

the permutations of AOs. For example, the structural matrix N corresponding to the tetrahedral system L_4
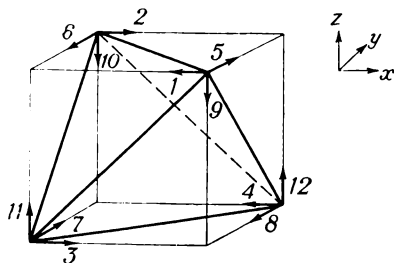

Fig. 36

whose each vertex accommodates three p-AO (Fig. 36) has the form

$$N = \begin{pmatrix}
0 & 1 & 1 & \varkappa & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 \\
1 & 0 & \varkappa & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
1 & \varkappa & 0 & 1 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 \\
\varkappa & 1 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 1 & \varkappa & 1 & 0 & 0 & 0 & 1 \\
1 & 0 & 0 & 0 & 1 & 0 & 1 & \varkappa & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 & \varkappa & 1 & 0 & 1 & 0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 & 1 & \varkappa & 1 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & \varkappa & 1 & 1 \\
0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & \varkappa & 0 & 1 & 1 \\
1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 1 & 0 & \varkappa \\
0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 1 & \varkappa & 0
\end{pmatrix}$$

Here the dimensionless parameter $\varkappa$ allows. for only the π interactions between ligands. The spectrum of eigenvalues of the matrix N and the corresponding IR groups T_d are given in Table 4.

Eigenvalues of matrix N	IR groups T_d
$x_1 = 4 + \varkappa$	A_1
$x_2 = 1 + \varkappa$	E
$x_3 = -1 - \varkappa$	T_1
$x_{4,5} = -\dfrac{1}{2} \pm \sqrt{\dfrac{17}{4} - 3\varkappa + \varkappa^2}$	T_2

From the data of Table 4 we obtain the following sequence of MO energies:

$$\varepsilon(a_1) < \varepsilon\,(t_2) < \varepsilon\,(e) < \varepsilon\,(t_1) < \varepsilon\,(t_2).$$

The calculations of tetrahedral systems (B_4H_4, $B_4H_4^{-2}$ etc.) confirm the result obtained.

Note that although the matrix N is of rather high dimension, it is more convenient to use it to get the qualitative and semiquantitative information than to calculate the energy levels directly by the quantum-mechanical methods because the matrix N is substantially "rarefied" with zero elements.

Topology of Molecular Charge Distributions

The development of chemistry has both led to, and been made possible by, the evolution of certain primary concepts. These concepts, without which there would be neither correlation nor prediction of the observations of descriptive chemistry, are: (1) the existence of atoms of functional groupings of atoms in molecules as evidenced by characteristic sets of properties; (2) the concept of bonding; and (3) the associated concepts of molecular structure and molecular shape. These concepts logically (but not historically) are consequences of fundamental

topological properties of the charge distribution (electronic and nuclear) in a molecular system. In terms of the Born-Oppenheimer approximation the electronic distribution $\rho\,(\vec{r})$ is the scalar field defined in the real three-dimensional space with Euclidean metric.

The universal topological properties of $\rho\,(\vec{r})$ are characterized by its gradient field $\nabla\rho\,(\vec{r})$. (See Fig. 37 showing the field $\rho\,(\vec{r})$ and the trajectories of its gradient in the B_2H_4 plane of diborane.)

Critical points. The properties of this field, and hence the principal characteristics of a charge distribution, are totally determined by the number and nature of its *critical points*, i.e. the points at which the field vanishes. Exactly, in the neighbourhood of the critical point $\vec{r}_c$

$$\nabla\rho\,(\vec{r})\Big|_{\vec{r}\,=\,\vec{r}_c} = 0.$$

K. Collard and G. Hall have demonstrated the utility of orthogonal trajectories, i.e. the paths traced by the gradient vectors of a scalar field. The gradient path direction is taken to coincide with that of growing $\rho\,(\vec{r})$ values. Only a single gradient path traverses any given point in space. All gradient paths are orthogonal to the isodensity (contour) lines. Also, all the paths originate and terminate at the critical points. Besides, Collard and Hall indicated that the properties of a critical point can be uniquely defined by two numbers, labelled rank and signature. R. F. W. Bader and coworkers have adopted them in their classification of charge distributions.

A bit of differential geometry... The set of nine second derivatives of $\rho\,(\vec{r})$

$$A_{ij} = \frac{\partial^2\rho}{\partial x_i\,\partial x_j}\ (i,\,j = 1,\,2,\,3)$$

forms a so-called Hessian matrix **A** (named after the German mathematician Ludwig Otto Hesse (1811-1874)) of $\rho\,(\vec{r})$ at the critical point. The properties of this point are determined by diagonalizing the Hessian matrix in the neighbourhood of $\vec{r}_c$. The *rank* of the critical point is equal to the number of nonzero eigenvalues of **A**. Usually the charge distributions in molecules possessing the equilibri-
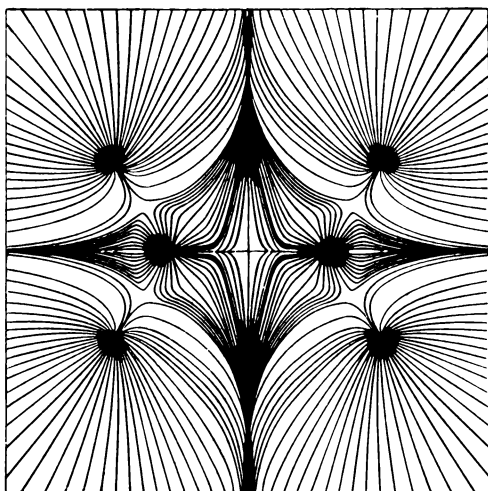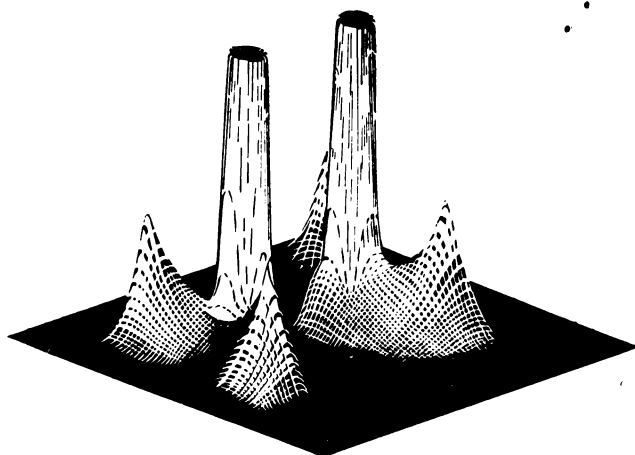
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Fig. 37

um nuclear configurations are characterized by the critical points of rank 3. The three eigenvalues determine the three orthogonal gradient paths that either originate or terminate at the critical point.

The *signature* is the number of excess positive eigen-values over negative ones.

Types of critical points. Graphically, the critical point is characterized by its phase portrait, i.e. the pattern of trajectories traced out by the gradient vectors in its
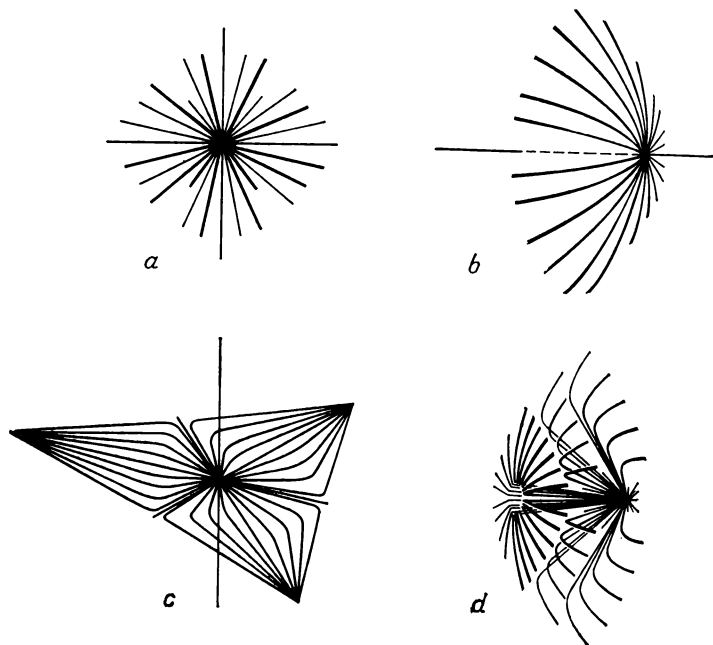

Fig. 38

neighbourhood. For critical points of rank three, four characteristic phase portraits are found, corresponding to the four possible signatures, —3, —1, +1, +3. Each of the four possibilities labelled as [rank, signature], e.g [3, —1], denotes the presence of a particular element of molecular structure.

A [3, —3] critical point. In this case all three eigen-values are negative and hence there is a local maximum in $\rho(\vec{r})$. All the gradient paths in the neighbourhood of a [3, —3] critical point terminate at that point (see Fig. 38a).

The maximum in ρ (r) at the position of a nucleus is not a true critical point as $\vec{\nabla}\rho$ $(\vec{r})$ does not vanish. However, near the nuclear cusp ρ $(\vec{r})$ behaves topologically as if it were a true [3, —3] critical point (see also Fig. 37).

A [3, —1] critical point. In this case ρ $(\vec{r})$ has a saddle point located between neighbouring atoms. All trajectories forming a surface terminate at the critical point (Fig. 38b). On this surface, the [3, —1] point has the properties of a two-dimensional maximum in ρ $(\vec{r})$, i.e. it behaves as a [2, —2] critical point. The eigenvector corresponding to the positive eigenvalue defines a unique axis for the [3, —1] point, which is perpendicular to the surface at the saddle point. The two gradient paths defining this axis *originate* at the critical point. These paths also define a line along which ρ $(\vec{r})$ is maximum with respect to the directions perpendicular to that line. Such a line is called a *bond path*.

It has been demonstrated that the network of bond paths defined by the unique axis of the [3, —1] critical points coincides with the network formed by linking together those pairs of atoms which are presumed to be bonded chemically.

Two remaining critical points... These points, [3, +1] and [3, +3], appear in actual molecular graphs. (According to R. Bader a molecular graph is a network of bond paths found for a given molecule.) If three or more nuclei form a ring of bonded atoms, then a [3, +1] point is to be found within the ring's perimeter. The associated ring surface is one on which ρ $(\vec{r})$ possesses a minimum value at the critical point [3, +1]; the gradient paths forming that surface originate at the saddle point [3, +1] (Fig. 38c). Figure 38d illustrates the phase portrait of an atom with a single neighbour (all trajectories terminate at the [3, —3] point).

If four or more nuclei form a bonded cage, a true three-dimensional minimum in ρ $(\vec{r})$ must exist inside that cage; all gradient paths within the cage originate at such a critical point.

The number and type of critical points of rank three which can coexist in a molecular system is governed by the

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following expression (the partial case of the Poincaré-Hopf relationship):

$$n - N + r - c = 1,$$

where n is the number of nuclei, i.e. the number of pseudo-[3, —3] critical points, N is the number of bonds, i.e. the number of [3, —1] critical points, r is the number of rings, i.e. of the [3, +1] critical points, and c is the number of bonded cages, i.e. of the [3, +3] critical points. For example, the (n, N, r, c) index characterizing the structure of P_4 is (4, 6, 4, 1) and of diborane (8, 8, 1, 0).

Clearly, the set of numbers (n, N, r, c) is a useful index of the major topological properties of a molecular charge distribution.

When structure is changed... The making and breaking of a chemical bond is topologically a discontinuous process, and the associated change in structure is therefore abrupt. It has been pointed out that the analysis of the discontinuous change in the topological characteristics of a molecular charge distribution resulting from the discontinuous change in the nuclear coordinates is given by the catastrophe theory of René Thom. However, the discussion of that theory lies outside the scope of our book.

Live Pages　　·
of the Past

In this chapter we shall tell of the origination of the graph theory and its first utilization for solving various chemical problems. At the same time we shall consider some present-day problems pertaining to chemical topology and having, as will be shown below, a long history.

Analysis Situs and Origination
of Graph Theory

Walk over Königsberg bridges. The need for the development of new «nonmetric» geometry was voiced first back in the 17th century. Thus, the great German mathematician and philosopher G. W. Leibniz wrote on September 8, 1679 in a letter to the Dutch physicist C. Huygens: "I am chagrinned with algebra because it provides neither short nor best ways to construct geometry, and I think therefore that we need still another analysis, properly geometrical ... permitting a *position* to be expressed just as directly as algebra expresses a *quantity*".

The historians disagree on what was actually meant by Leibniz, whether it was what later became topology, or the branch of mathematics called vector analysis. Everybody is unanimous, however, concerning one thing: the origination of topology and the graph theory is associated with the work of the great mathematician of the 18th century Leonard Euler (1707-1783), a Swiss who lived in Russia for a long time and who made significant contributions to various branches of pure and applied mathematics. During his lifetime, half of which he was absolute-

ly blind, „Euler published 530 books and articles and after his death, the remaining manuscripts were being published for almost 50 years more, so that the total number of his works approached 900.

The article that is of interest to us now was submitted by Euler to the St. Petersburg Academy of Sciences on August 26, 1735. Wrote Euler: "In addition to that part of geometry where magnitudes are treated and which was zealously elaborated at all times, there is another, quite unknown so far, part of geometry to which Leibniz alluded for the first time, calling it geometry of position.... I believe it will be useful to demonstrate here as an example of geometry of position a method I found to solve problems of that kind .... One of such problems which is well known boils down to the following.

In the city of Königsberg, East Prussia, there is an island named Kneiphoff. It is surrounded by a bifurcating
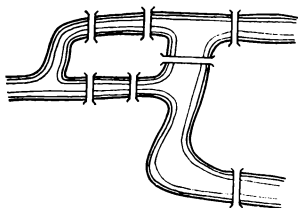

Fig. 39

river spanned by seven bridges (Fig. 39). The question is whether one can walk over all bridges crossing each of them only once."

Euler proved such a stroll over Königsberg bridges impossible. Moreover, he generalized his conclusion, having demonstrated that the required itinerary exists only for the connected graph each of whose vertices is incident to an even number of edges. As to the graph representing the problem of Königsberg bridges (Fig. 40), it is connected, but its vertices are of only odd degrees.

Euler proved another topological theorem (1750, published in 1758) named after him: for every convex polyhedron homeomorphic to a sphere,

$$\mathscr{B} - \mathscr{P} + \mathscr{T} = 2,$$

where $\mathscr{B}$ is the number of vertices, $\mathscr{P}$ the number of edges, and $\mathscr{T}$ the number of faces.

To some of our readers this formula may remind Gibbs' phase rule

$$f - k + r = 2,$$

where f is the variance of the system, i.e. the number of independent variables specifying its state (pressure, tem-
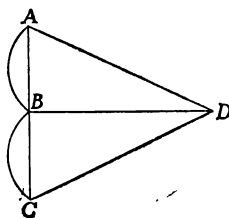

Fig. 40

perature, component concentrations of all phases); k is the number of components, and r is the number of phases of the system.

The phase rule plays an important part in chemistry. For example, it helps to answer the controversial question of long standing: whether the solubility of solids in liquids depends only on temperature, or also on pressure. Inasmuch as such a system is composed of two phases (liquid solution and a solid) and two components (solvent and solute), then

$$f = 2 + 2 - 2 = 2.$$

Thus, the considered system is divariant, and the solubility depends on two variables, temperature and pressure.

Graphs and electricity. After Euler the graph theory was rediscovered several times. In 1847 G. Kirchhoff developed the theory of trees to solve the problem about currents flowing in each conductor and in each loop of an electric circuit. Kirchhoff replaced the electric circuit by the graph and developed the procedure to solve the system of equations defining the current intensity, analysing only the so-called skeleton trees of the initial graph.

A few words on terminology. In the 19th century the great contributors to the development of the graph theory were many eminent mathematicians: A. Cayley (see below), K. Jordan, J. J. Sylvester and others. At the same time, J. B. Listing, F. Klein, A. Möbius, B. Riemann, A. Poincaré and others developed topological methods in their works. The term "topology" itself was introduced in 1836 by J. Listing, but was put into practical use only in the late 20s of the 20th century; up to that time the Latin term *analysis situs* was preferred ("analysis of position"), which is traced back to Leibniz.

However, before mathematical methods could be employed in chemistry, the latter had to reach sufficient theoretical maturity. Thus, the graph theory and some other divisions of discrete mathematics could be applied to the solution of chemical problems only after the chemical structure theory had emerged. In the next section we shall briefly discuss some important landmarks in the development of ideas concerning the structure of chemical compounds.

From Ideograms to Structural Formulas

Symbol of substance. Since ancient times people have used various symbols for conventional description of real objects and phenomena. On the walls and columns of old Egyptian temples one can see the signs of water, gold, silver, etc. Figure 41 shows the signs that were used by three ancient civilizations, Chinese, Egyptian, and Greek, to denote water and alum. These signs are of different nature; sometimes they "picture" a substance or some of its properties (see, e.g., the Egyptian sign for water), whereas in other cases ideograms convey some secret meaning which is often very difficult to decipher.

The ideographic signs were used by medieval alchemists although sometimes they resorted to letter abbreviations (Latin, as a rule) of substances. The medieval nomenclature was very jumbled. At the end of the 18th century the Swedish chemist T. O. Bergman (1735-1784) and the French scientists A. F. Fourcroy, L. B. Guyton de Morveu, and A. L. Lavoisier proposed to put it in order. However, for some reasons, that we are not able to discuss now,

their system had not become popular. The descriptive
signs of some compounds and the chemical reaction sym-

Country	Symbol of water	Symbol of alum
China		
Egypt		
Greece		

Fig. 41

bols used by the French chemists were very complex and
ambiguous.

An interesting version of graphical notation for chemi-
cal formulas was proposed by the English scientist
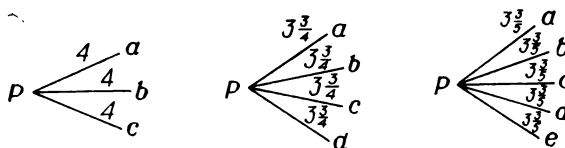W. Higgins. Figure 42 illustrates the formulas for some

Fig. 42

nitrogen oxides, taken from his treatise *A Comparative
View of the Phlogistic and Anti-Phlogistic Theories* pub-
lished in London in 1789. The symbol P denotes nitrogen,
and the symbols a, b, c, etc., oxygen atoms. The numbers
indicate the atomic interaction intensities. To each atom
Higgins assigned three conditional "force units". Then the
total force of atomic interaction equals $3n$, where n is
the number of atoms in the molecule, and the value
$3n/k$ is alloted to each bond (k is the number of bonds).
It should be noted that Higgins had not defined the term

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"bond", it was introduced into science only three quarters of a century later.

Emergence of chemical atomism. The beginning of the 19th century was marked by the emergence of atomic theory developed by the famous English scientist John Dalton (1766-1844). According to Dalton, atoms combine in multiple proportions. Thus, if two atoms form only one compound, they associate in the 1 : 1 ratio; if two atoms form two compounds, their ratios in these compounds are respectively 1 : 1 and 1 : 2, and so on. Accordingly, Dalton adopted the formula HO for water, CO for carbon monoxide, CO_2 for carbon dioxide, and so on. From these formulas he determined the atomic masses of elements. It is clear that frequently both atomic masses and chemical formulas of Dalton were not correct.

Besides, Dalton proposed new symbols for chemical elements, as well as a new way of graphic representation of compounds. Some of the symbols and formulas taken from his treatise *A New System of Chemical Philosophy* (1808) are shown in Fig. 43. Note that Dalton sought
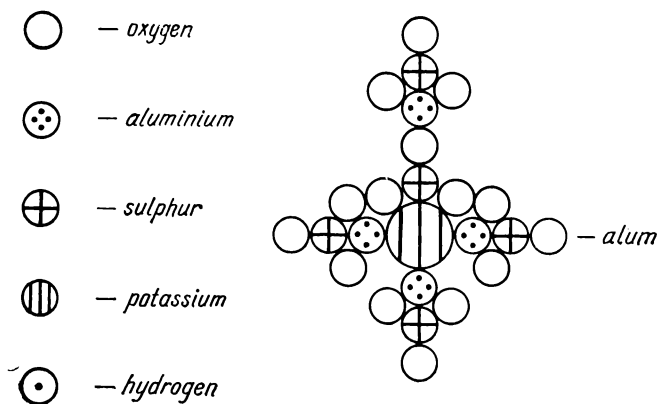

Fig. 43

to present his graphical formulas in the most ordinary and symmetric fashion.

Later the Dalton method of determining the formulas of chemical compounds was castigated by the greatest Swedish chemist J. J. Berzelius (1779-1848)*.

However, the method of determining the element composition of substance, proposed by Berzelius, also failed because the reliable methods of determining molecular masses had not been elaborated yet. The existing methods, as a rule, led to confusion resulting in its turn in subsequent numerous errors in determining the molecular masses of the whole classes of organic compounds.

The first adequate method of determining molecular masses was the method based on the measurements of vapour density of a substance. That method was a direct consequence of the Avogadro molecular theory developed in 1811-1821. However, the ideas of the Italian scientist were recognized only after the congress of chemists in Karlsruhe (1860), primarily due to the efforts of his compatriot S. Cannizzaro. The latter completed reforming Dalton's atomic theory and opened the way to the emergence of the chemical structure theory. That theory, as well as many significant concepts of structural chemistry (e.g. valence, or chemical bonding), could appear only when an end was put to the confusion and arbitrariness in derivations of chemical formulas and determinations of molecular masses. But the structural theories which appeared before the 60s of the last century were still marked with the imperfection of the earlier atomic concepts.

Variation on four themes. The most significant of these theories is the theory of types proposed by the eminent French chemist Ch. Gerhardt (1816-1856) in 1853. According to Gerhardt, each organic compound belongs to one of four "types": H_2, HCl, H_2O, and NH_3. Replacing hydrogen in them by various radicals, one can obtain hydrocarbons (H_2 type), alcohols, ethers, acids (H_2O type), etc. On the basis of his theory Gerhardt developed a harmonious systematization of organic compounds, using extensively the concept of homology; he also predicted, and at a later date synthesized, a number of anhydrides of monobasic acids. However, as the German chemist

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* Besides, in 1813-14 Berzelius proposed the letter designations of elements which on the whole are used even now.

H. Kolbe aptly noted, "nature does not limit itself with performing variations on four themes: water, hydrogen, hydrogen chloride, and ammonia". In fact, the number of types had to be later considerably increased, so that the theory had lost much of its initial simplicity and clearness. Moreover, it could not cover many facts related to the addition and elimination reactions and to isomerism.

Kekulé's formulas. In 1857 the German chemist A. Kekulé deduced that oxygen was bivalent, nitrogen and phosphorus trivalent, and, what is most important, carbon tetravalent. He regarded valence as the number of

Fig. 44

"affinity units" capable of mutual saturation when atoms combine into a molecule. Similar ideas were developed by H. Kolbe (1875) and the English chemist E. Frankland (1852).

Figure 44 is a graphic representation of methyl ether of formic acid according to Kekulé (1859).

Referring to his formulas, Kekulé warned that they do not express either the spatial distribution of atoms or any metric properties of molecules; the formulas only described the "relationship of binding atoms".

Three aspects of chemical structure theory. By the middle of the 19th century the time was ripe for radical changes in organic chemistry since none of the contemporary theories could generalize the tremendous amount of accumulated experimental data. And the new theory was not long in appearing. It appeared in 1861; that was the theory of chemical structure produced by A. M. Butlerov.

The term "chemical structure" was defined by the Russian scientist in different ways; first, as "chemical" bonding or mode of mutual binding of atoms in a complex body", later, as "distribution of action of affinity a certain amount of which is possessed by each chemical atom", and still later, as "mode of mutual chemical bonding of elementary atoms in a molecule". In their essence, all these

definitions are quite similar. In modern scientific terms, Butlerov represented every chemical compound as a topological graph, having associated the properties of a molecule, its "chemical nature", with "the nature of elementary constituents, their number and chemical structure". Butlerov especially emphasized the thesis about reciprocal influence of atoms in a molecule.

An important aspect in the development of the chemical structure theory was its extension to unsaturated compounds. In 1870 Butlerov demonstrated that the concept of multiple bonding formulated earlier by A. Crum Brown and E. Erlenmeyer and furnished an adequate interpretation to all cases of isomerism, known at that time, in the unsaturated compound series. The introduction of the multiple bonding concept into structural chemistry made it possible in many cases to solve the problem of distribution of "the power of chemical affinity" among atoms.

Thus, we can distinguish at least three aspects of the chemical structure theory:

(1) *topological* aspect, when neither the multiplicity of chemical bonding, nor any of its energy or geometric characteristics, and reciprocal influence of atoms are considered; only the topological graph of a molecule is specified;

(2) mixed *valence-and-topological* aspect, when the notion of chemical bonding is generally characterized by indicating its multiplicity, taking into account formal valencies of atoms; molecules are thus represented as graphs with multiple edges;

(3) *proper chemical* aspect, when individual characteristics of atoms in a molecule, their reciprocal influence, specific nature of bonds, etc. are taken into consideration.

Riddle of isomerism. The chemical structure theory made it possible to solve many urgent problems of chemistry of that time, in particular the problem of isomerism. The vestiges of ideas about isomerism can be found in the atomist theories of philosophers of Ancient Greece. Many years later, in the 18th and the beginning of the 19th century, some scientists (J. Jungius, J. Dalton, A. von Humboldt) advanced the theory of the existence of substances of identical composition, but possessing different properties due to different arrangement of atoms in their molecules. In 1811 the French physicist and chem-

ist J. Gay-Lussac proved experimentally the existence of isomers. However, the isomerism concept was introduced into chemistry only in 1830s by Berzelius who defined isomers (from Greek ισος, equal, and μερος, a part, share) as "substances possessing identical chemical composition and molecular weight, but different properties".

The underlying cause of isomerism was disclosed only after the structure theory was produced. Owing to the work of Butlerov and his followers the isomers of various classes of organic compounds, alkanes, olefins, alcohols, etc., were investigated. In 1867 the German chemist W. Körner, a student of A. Kekulé, introduced the terms ortho-, meta-, and para-isomer for disubstituted derivatives of benzene.

By the middle of 1870s the problem of the number of isomers for a compound of a given composition acquired more significance, having engaged the attention of both chemists and mathematicians.

Mathematics of Structural Formulas

Pioneer. One of the first mathematicians who paid attention to the chemical structure theory was the outstanding English scientist Arthur Cayley. In 1875 he employed the graph-theoretical methods for solving the problem of counting isomers of C_nH_{2n+2} alkanes with the given n. Initially, Cayley tried to derive the general formula for determining the number of such isomers each of which he represented as a topological graph (a tree, to be more exact). These attempts, however, failed. Then using the results of his earlier 1857-59 investigations, Cayley developed the method of counting so-called *rooted trees* with n vertices. A tree is called rooted if one of its vertices is marked, for example, somehow coloured. Figure 45 shows nine rooted trees with five vertices ($n = 5$)*. Then Cayley divided the set of rooted trees into two groups, centric and bicentric trees.

The *centre* of a graph is such a vertex v whose maximum distance from any other vertex is the least of all possible distances. Figure 46 illustrates centric and bicentric trees.

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* To satisfy the requirement for carbon to be tetravalent, Cayley considered only the trees whose vertices have the degrees not exceeding four.

Let us get back to our example ($n = 5$). Among nine trees pictured in Fig. 45 there are five centric trees, a, d, e, g, h (the centre of the graph may not coincide with the coloured vertex), and four bicentric ones, b, c, f, i.
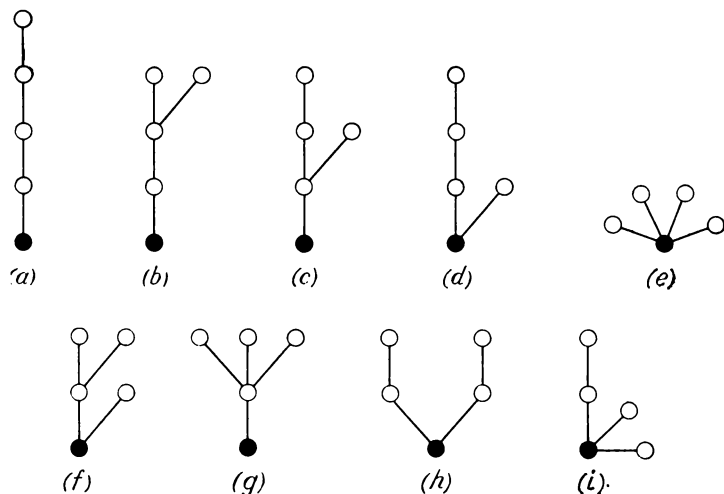

(a)　　　(b)　　　(c)　　　(d)　　　(e)

(f)　　　(g)　　　(h)　　　(i).

Fig. 45

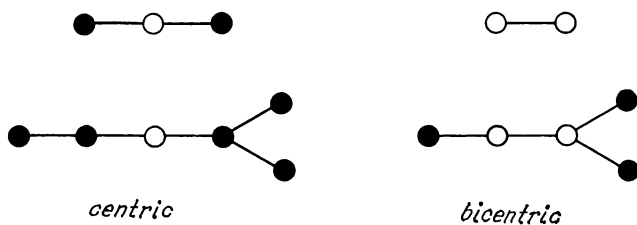It is easy to see that all bicentric trees are isomorphic (the fact that one of the vertices is coloured is not taken

centric   bicentric

Fig. 46

into account). As to the five centric trees, a, d, h and e, g are isomorphic within each group.

Thus, the set of nine rooted trees with five vertices can be subdivided into two subsets of nonisomorphic centric trees and one subset of bicentric trees. According to Cay-

ley, the total number of isomers of saturated C_5H_{12} hydrocarbons is equal to the total number of nonisomorphic rooted trees, i.e. 3 (=2 + 1).

Table 5

n	Number of nonisomorphic trees		Number of alkane isomers	
	centric	bicentric	according to Cayley (1875)	present-day data
1	1	0	1	1
2	0	1	1	1
3	1	0	1	1
4	1	1	2	2
5	2	1	3	3
6	2	3	5	5
7	6	3	9	9
8	9	9	18	18
9	20	15	35	35
10	37	38	75	75
11	86	73	159	159
12	183	174	357	355
13	419	380	799	802

In Table 5 Cayley's results for the first 13 members of the homological series of alkanes are compared to the present-day data. As is seen from the table, Cayley's method provides erroneous results beginning with $n = 12$.

Beachhead. However, basically this discrepancy does not disparage the explorations of the English mathematician. Cayley was the first to represent a molecule as a topological graph and to start developing the methods of isomer enumeration on the basis of the graph theory. Moreover, Cayley forwarded the notion of enumerative polynomial for rooted trees, i.e. the polynomial whose coefficients A_i specify the number of rooted trees with i vertices:

$$1 + A_1 x + A_2 x^2 + \ldots$$

The abstract of Cayley's paper devoted to enumerating alkane isomers was submitted to the German Chemical society (Deutschen chemischen Gesellschaft) by the eminent German chemist C. Schorlemmer and was published

in Berichte der Deutschen chemischen Gesellschaft; the paper attracted the attention of both chemists and mathematicians.

Later, beginning with 1930s analytical methods of finding the coefficients A_i were elaborated*. But, as it was noted by the greatest expert in the graph theory F. Harary, "the methods of enumeration in combinatorial analysis may be regarded rather as art than as science".

A. Cayley was also the creator of the matrix theory; he made an essential contribution to the development of the group theory, i.e. those branches of mathematics which were later extensively used in physics and mathematics. Moreover, Cayley was the first to indicate the relationship between the point groups of symmetry and the permutation groups (see Chapter 6).

Cayley's theorem states:

Any finite group G of order n is isomorphic to a certain subgroup of the permutation group S_n.

Note that the considered group G of the n-th order is isomorphic not to the group S_n itself but to its subgroup, since S_n contains more elements than G does. For example, the symmetry group of an equilateral triangle C_{3v} includes six symmetry operations $(E, C_3, C_3^2, 3\sigma_v)$ whereas the group S_6 includes 6! permutations. Consequently, C_{3v} and S_6 are not isomorphic, but the groups C_{3v} and S_3 are.

Since 1928 permutation groups have been extensively used in quantum mechanics of poly-electronic systems (atoms, molecules, solids) and during the last decade they, together with the graph theory, found application in the theoretical treatment of some intramolecular rearrangements. Due to the significance and obvious usefulness of the results obtained thereby, we shall discontinue for a while the chronological sequence of presentation and tell of certain methods of description of spatially nonrigid compounds.

Ligands in Motion

The study of some nonrigid molecules carried out during the last 20 years or so revealed various intramole-

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cular rearrangements of ligands taking place in such molecules and resulting in the ligand interchange which occurs without a break of their bonding with the central
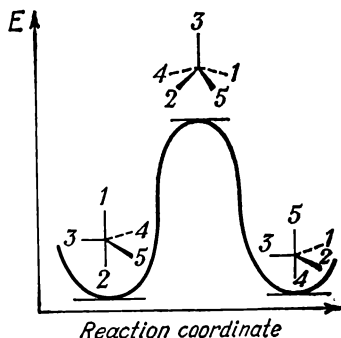

Fig. 47

atom. Various mechanisms of such a ligand interchange were suggested. An example is provided by so-called...

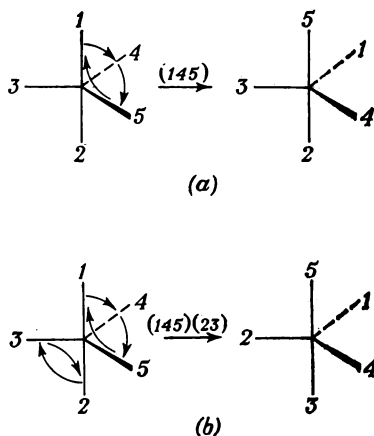Berry's pseudorotation. In the case of a trigonal bipyramid molecule, e.g. PF_5, this mechanism consists in an

Fig. 48

interchange of two equatorial ligands with two apical ones, with the third equatorial ligand keeping its position. Due to such a rearrangement the molecule rotates in

гace, hence the term "pseudorotation". Figure 47 shows energy variation vs the reaction coordinate in the process of Berry's pseudorotation. The peak in the curve corresponds to the transition state with tetragonal pyramid configuration. In many penta-coordination compounds the energy barrier is low and can be overcome at higher temperatures.

The pseudorotation phenomenon is vital to structural chemistry of phosphorus, silicon, transitional metals, and some other elements. Apart from pseudorotation, there are other rearrangement mechanisms, for example, trigonal twist (Fig. 48a) examined in dynamic stereochemistry of icosahedral carboranes, "tourniquet" mechanism (Fig. 48b), etc.

The theoretical investigation of these reactions requires quantum-mechanical methods, in particular, the study of chemical bonds in initial, final, and intermediate compounds, as well as the consideration of nuclear motions. Yet frequently the important information can be obtained without analysis of electronic structure of molecules and investigation of actual motion of nuclei, only resorting to the graph theory and employing the group-theoretical conceptions. Here we should define two terms: *permutation isomers* and *permutation isomerism reaction*.

Permutation isomers are identified as the compounds having the same qualitative and quantitative composition, the identical set of ligands, the identical molecular skeleton, and differing only by the distributions of ligands over skeletal positions in the molecule*.

Let us label the ligands: $\{l_1, l_2, \ldots, l_n\}$ and the skeletal positions in the molecule: $\{s_1, s_2, \ldots, s_n\}$. Then each permutation isomer will have a corresponding $(2 \times \times n)$ matrix:

$$\binom{l}{s} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & \ldots & n \\ i & j & k & t & u & \ldots & m \end{pmatrix}.$$

The first row of the matrix consists of ligand indices (numbers) written in the growing order, and the second

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* The term "skeletal position" refers to the "place" in the vicinity of the central atom at which a ligand can be found.

one of indices (numbers) of skeletal positions. As an example, let us consider a trigonal bipyramid system with a definite enumeration of skeletal positions:
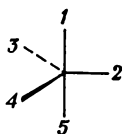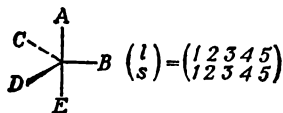

Denote five ligands as follows: l_1 as A, l_2 as B, l_3 as C, l_4 as D, and l_5 as E. Then the permutation isomer
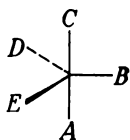
will be represented by the matrix

$$\binom{l}{s} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 5 & 2 & 1 & 3 & 4 \end{pmatrix}$$

implying that the first ligand (A) is in the fifth position, the second (B) in the second, the third (C) in the first and so on. The isomer of the type

 $\quad \binom{l}{s} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 1 & 2 & 3 & 4 & 5 \end{pmatrix}$

is adopted as the standard one.

When one permutation isomer of a certain molecule turns into another, differing from the first one, we say that the permutation isomerism reaction takes place.

The following rearrangement may serve as an example of such a reaction:
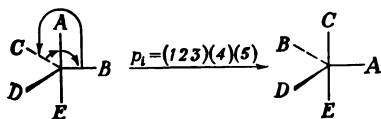
The symbol $p_i = (123)$ (4) (5) denotes a rearrangement that brings the ligand that resided initially at position 1 to position 2, the ligand that resided initially at position 2 to position 3, and the one that was at position 3 to position 1. Such a cyclic permutation is designated by the symbol (123). This expression is referred to as a *cycle*. The length of a cycle, i.e. the number of elements in it, is equal to 3 here. Cycles of unitary length imply that the ligands residing at positions indicated do not change these positions as the reaction proceeds. In our case the ligands at positions 4 and 5 do not shift anywhere (cycles (4) and (5)). It should be noted that the arrows pointing to the ligand displacement direction are conditional and may not correspond to the actual rearrangement mechanism, the latter can be determined either experimentally, or theoretically, by quantum-mechanical methods.

Why weaving a tangled web? the reader may wonder. It is well-known that n objects can be permutated in $n!$ ways. Is it not simpler to write out all possible permutations of ligands (no trouble if n is large: a computer will help out) and then to distinguish those with the lowest activation barriers?

This can be done only if a molecule has no symmetry elements. But in most cases the number of different reactions of permutation isomerism is less than $n!$. And there are definite reasons for that.

First, some permutations correspond to the rotation of a molecule about one of its symmetry axes, for example,
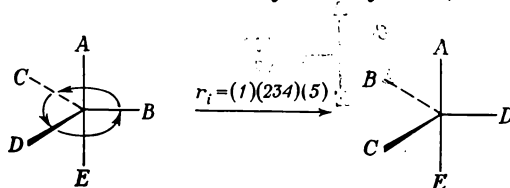

and do not lead to permutation isomerism reactions because in these cases a molecule just turns in space.

The set of all permutations involving the series of indices of skeletal positions and corresponding to the rotation of a molecule as a whole forms a group (denoted usually by R) which is actually a subgroup of group S_n of all permutations of n ligands.

Any symmetry operation (rotation as well as reflection) can be associated with a certain permutation. In other words, the symmetry operations of the molecular point group G generate a permutation group of skeletal position indices (G_S). Note that G_S is also as a rule nonisomorphic to the group S_n (see above).

Second, if all ligands are identical in their nature and differ only in their numbers, all possible isomerism reactions prove to be indistinguishable due to the symmetry of a molecule.

Nevertheless such permutations can be distinguished, for example, using the method of nuclear magnetic resonance (NMR), e.g. the geometry of a phosphorus pentafluoride molecule was found by the electron diffraction method and from the analysis of IR spectra:
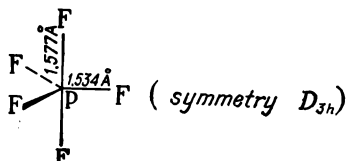
However, the detailed studies of NMR spectra led to the conclusion about the interchange of apical and equatorial fluorine atoms. Since the apical and equatorial bonds P—F in PF_5 have different lengths, the NMR spectrum can be expected to consist of two doublets with integral intensity ratio 2 : 3. Actually, the observed NMR spectrum of PF_5 (at ^{19}F) has one doublet caused by spin-spin interaction of P and F nuclei, i.e. the splitting of signals from axial and equatorial fluorine atoms is absent.

Thus, far from all permutations can be treated as permutation isomerism reactions. The distinguishable permutations should be selected. The criterion of indistinguishable permutations of ligands was proposed in 1971 by the American chemist W. G. Klemperer; it can be stated as follows:
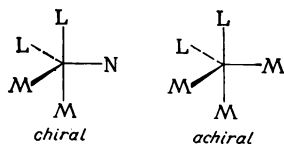
Two permutation isomerism reactions p_n and p_m are indistinguishable (identical) in the case of completely symmetrical (achiral) surrounding of the central atom if for a certain permutation $g_i \in G_S$ the equality

$$p_n = g_i^{-1} p_m g_i \qquad (36)$$

holds,

Otherwise the reactions p_n and p_m can be distinguished.

What is chirality? The term *chirality* denotes the property of a molecule to be nonidentical to its mirror image. All coordination polyhedrons with identical ligands are achiral. When the ligands are different, the chiral compounds may be formed. Thus, a tetrahedron with four different ligands is chiral. A trigonal bipyramid and tetragonal pyramid may be (but not necessarily will be) chiral if three (or more) ligands are of different types, e.g.

Subsequently we shall confine ourselves to the case of intramolecular isomerism in achiral molecules.

Figure 49 illustrates the relationship between two indistinguishable (according to Klemperer) permutation isomerism reactions [$g_i = (1) (234) (5)$ represents the rotation about the axis C_3 passing through the ligands AE].

Counting indistinguishable reactions. The number of indistinguishable reactions is determined by means of the enumeration polynomial whose coefficients are calculated by the graph-theoretical methods and the methods of permutation group theory. We cannot describe here the procedure of finding the coefficients of the enumeration polynomial, and so we shall consider only several concepts that are necessary for translation of mathematical results into the language of chemistry.

The set of permutations $\{p_i\}$ satisfying the condition (36) forms the coset of the group S_n (and its subgroup G_s). The total number of such cosets minus the number of sets consisting of the elements of group R is equal to the number of formally distinguishable permutation isomerism reactions for an achiral molecule.

It can be demonstrated that permutations relating to the same class have the same cycle structure, or expressed otherwise, are of the same cycle type. The following

example • may serve as an illustration: two symmetry operations C_3 of group D_{3h} correspond to two permutations of the same class:

$$(1)\ (2\ 3\ 4)\ (5)$$
$$(1)\ (2\ 4\ 3)\ (5)$$

Both of them contain two cycles of unitary length and one cycle of length 3 each. The cycle structure of these permutations is expressed by the symbol $(2, 0, 1, 0, 0)$, where the ordinal number of the digit in parentheses coincides with the cycle length and its magnitude with the number of cycles of a given length. In the symbol $(2, 0, 1, 0, 0)$ the *first* place is occupied by digit *two* because both permutations contain *two* cycles of *unitary* length each and so on. In the general case the cycle structure symbol of permutations of a given class has the form: $(j_1, j_2, \ldots, j_n)$, where j_1 is the number of cycles of length 1, j_2 is the number of cycles of length 2, etc. Each distinguishable permutation isomerism reaction belongs to its specific class and cycle type.

Now we can write the enumeration polynomial F in the general form defining the permutation isomerism reactions:

$$F = \sum_{(j_1, j_2, \ldots, j_n)} A'_{j_1, j_2, \ldots, j_n} a_1^{j_1} a_2^{j_2} \ldots a_n^{j_n}, \qquad (37)$$

where $A'_{j_1, j_2, \ldots, j_n}$ is the number of distinguishable reactions of cyclic type $(j_1, j_2, \ldots, j_n)$; the prime signifies

$$(14)(2)(3)(5) = p_n$$
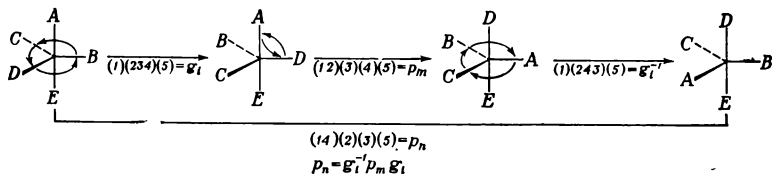$$p_n = g_i^{-1} p_m g_i$$

Fig. 49

that the permutations corresponding to the rotation of the molecule as a whole are not taken into account; a_i are certain conditional variables; summation is carried out over all cyclic types.
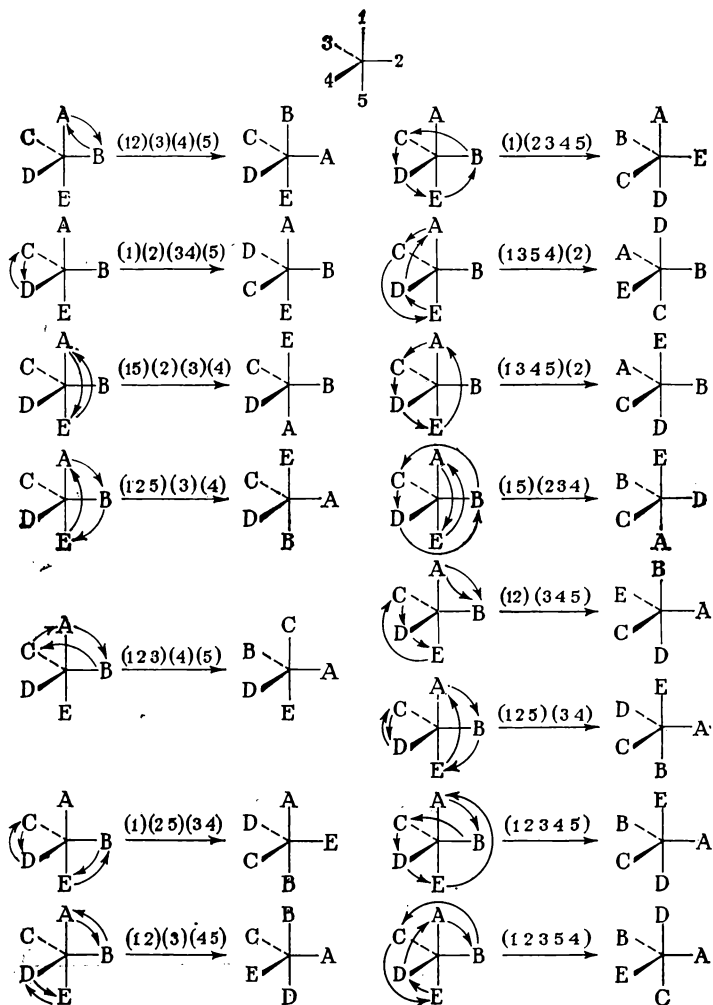
Fig. 50

Using the graph enumeration methods (so-called Pó-
lya's theorem), Klemperer derived F for the case of
achiral trigonal bipyramid molecule (D_{3h}) in the form

$$F = 3a_1^3a_2^1 + 2a_1^2a_3^1 + 2a_1^1a_2^2 + 3a_1^1a_4^1 + 3a_2^1a_3^1 + 2a_5^1 \quad (38)$$

Let us "decipher" this expression. As an example, let us consider the first term $3a_1^3a_2^1$. The subscript (i) of the variable a_i^k denotes the cycle length, the superscript (k) the number of cycles of length i. Then the first term in the expression (38) means that there are three different permutations of cyclic type (3, 1, 0, 0, 0).

Figure 50 shows all 15 distinguishable permutation isomerism reactions for achiral pentacoordination molecule of symmetry D_{3h}.

Klemperer examined the other cases as well: (1) when the molecule is chiral, and (2) when the molecule (either chiral or achiral) is not fixed in a crystal lattice but performs rotations and displacements (in fluids).

Thus, valuable information concerning the possible nature of permutation isomerism reactions was obtained only by the methods of the graph theory and group theory, without analysis of electronic and nuclear densities.

Cayley's Followers

The works of A. Cayley on isomer enumeration had drawn attention of many chemists and mathematicians. In 1882 Cayley delivered in the USA a series of lectures on application of mathematics in structural chemistry. A few years earlier, in 1878, the English mathematician J. J. Sylvester who founded the first mathematical journal in America (Amer. J. Math.) published in it an article dealing with the application of algebraic methods in the valence theory. True, Sylvester was not occupied with the problem of isomer enumeration. His investigations taken up later in 1901-1904, by P. Gordan in Germany and V. G. Alekseev in Russia laid a foundation for the spin valence theory created a quarter of a century later. The authors of that theory (W. Heitler, F. London, M. Born, H. Weyl, Yu. B. Rumer, and others) were familiar with the investigations of Sylvester, Gordan, and Alekseev and made use of their results, having filled them with quantum-mechanical content.

As to isomer enumeration, the various attempts made in the 19th century to develop the Cayley approach any further failed. Only in 1930s the American scientists H. R. Henze and C. M. Blair derived the formulas for determination of the number of isomers in aliphatic com-

pounds of certain homological series. The solution of the problem discussed here was greatly promoted by the discovery of the so-called enumeration theorem of Pólya in 1937*.

Pólya's theorem and benzene derivatives. Since the theorem is very complicated we cannot present it here, we shall analyse only one important partial case, the enumeration of isomers of substituted benzene derivatives.

Table 6 shows the relationship between the symmetry group operations of topological graph of a benzene molecule and permutations of their vertices; the cyclic type of each permutation is also indicated. Using the data of this table, we can obtain the following expression similar to (37):

$$Z\,(C_6H_6) = 1/g \sum_{(j_1,\ldots,j_n)} a_1^{j_1} a_2^{j_2}, \ldots, a_n^{j_n},$$

where g is the order of the group, i.e. the number of elements in the group. For the symmetry group of the topological graph of benzene $g = 12$. Therefore, in this case

$$Z\,(C_6H_6) = 1/12\,\{a_1^6 + 2a_6^1 + 2a_3^2 + 3a_1^2 a_2^2 + 4a_2^3\}. \tag{39}$$

To determine the number of isomers of substituted benzene derivatives (the substituting group is assumed to be monovalent) using Pólya's theorem, a change of the variables must be performed in expression (39)

$$a_n^{jn} \rightarrow (1 + x^n)^{jn},$$

i.e.

$$a_1^6 \rightarrow (1 + x)^6,$$
$$a_2^3 \rightarrow (1 + x^2)^3,$$
$$a_1^2 a_2^2 \rightarrow (1 + x)^2\,(1 + x^2)^2, \text{ etc.}$$

After simple calculations we obtain the following enumeration polynomial

$$1 + x + 3x^2 + 3x^3 + 3x^4 + x^5 + x^6,$$

---

* In a more partial formulation this theorem was given by mathematician D. Redfield (1927) and independently by chemists A. Lann and J. Senior (1929).

*

*

Table 6

Symmetry operation of topological graph of benzene	Permutation of vertices of topological graph of benzene	Cyclic type of permutation
E	$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 1 & 2 & 3 & 4 & 5 & 6 \end{pmatrix} = (1)\,(2)\,(3)\,(4)\,(5)\,(6)$	$(6,\ 0,\ 0,\ 0,\ 0,\ 0)$
C_6^+	$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 6 & 1 & 2 & 3 & 4 & 5 \end{pmatrix} = (1\ 6\ 5\ 4\ 3\ 2)$	$(0,\ 0,\ 0,\ 0,\ 0,\ 1)$
C_6^-	$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 2 & 3 & 4 & 5 & 6 & 1 \end{pmatrix} = (1\ 2\ 3\ 4\ 5\ 6)$	$(0,\ 0,\ 0,\ 0,\ 0,\ 1)$
C_3^+	$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 5 & 6 & 1 & 2 & 3 & 4 \end{pmatrix} = (1\ 5\ 3)\ (2\ 6\ 4)$	$(0,\ 0,\ 2,\ 0,\ 0,\ 0)$
C_3^-	$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 3 & 4 & 5 & 6 & 1 & 2 \end{pmatrix} = (1\ 3\ 5)\ (2\ 4\ 6)$	$(0,\ 0,\ 2,\ 0,\ 0,\ 0)$
C_2	$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 4 & 5 & 6 & 1 & 2 & 3 \end{pmatrix} = (1\ 4)\ (2\ 5)\ \ (3\ 6)$	$(0,\ 3,\ 0,\ 0,\ 0,\ 0)$
$\sigma_v^{(1)}$	$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 1 & 6 & 5 & 4 & 3 & 2 \end{pmatrix} = (1)\ (2\ 6)\ (3\ 5)\,(4)$	$(2,\ 2,\ 0,\ 0,\ 0,\ 0)$
$\sigma_v^{(2)}$	$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 5 & 4 & 3 & 2 & 1 & 6 \end{pmatrix} = (1\ 5)\ (2\ 4)\,(3)\,(6)$	$(2,\ 2,\ 0,\ 0,\ 0,\ 0)$
$\sigma_v^{(3)}$	$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 3 & 2 & 1 & 6 & 5 & 4 \end{pmatrix} = (1\ 3)\ (2)\ (4\ 6)\,(5)$	$(2,\ 2,\ 0,\ 0,\ 0,\ 0)$
$\sigma_v^{(4)}$	$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 6 & 5 & 4 & 3 & 2 & 1 \end{pmatrix} = (1\ 6)\ (2\ 5)\ \ (3\ 4)$	$(0,\ 3,\ 0,\ 0,\ 0,\ 0)$
$\sigma_v^{(5)}$	$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 2 & 1 & 6 & 5 & 4 & 3 \end{pmatrix} = (1\ 2)\ (3\ 6)\ (4\ 5)$	$(0,\ 3,\ 0,\ 0,\ 0,\ 0)$
$\sigma_v^{(6)}$	$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 4 & 3 & 2 & 1 & 6 & 5 \end{pmatrix} = (1\ 4)\ (2\ 3)\ (5\ 6)$	$(0,\ 3,\ 0,\ 0,\ 0,\ 0)$

in which the exponent of x is equal to the number of mono-valent groups bonded to the benzene ring, and the corresponding coefficient indicates the number of isomers. Thus, the term $3x^2$ indicates that there must be three disubstituted benzene derivatives (Fig. 51).

Foresight of the Russian chemist. In connection with the problem considered above we would like to make one remark. In 1870-80s in chemical literature, primarily in Russian, the chemical structure theory was a controversial

subject provoking much discord. The leading opponent of A. M. Butlerov was N. A. Menshutkin. D. I. Mendeleev also criticized the structure theory. They both preferred the so-called substitution theory originating from the theory of types of Gerhardt.
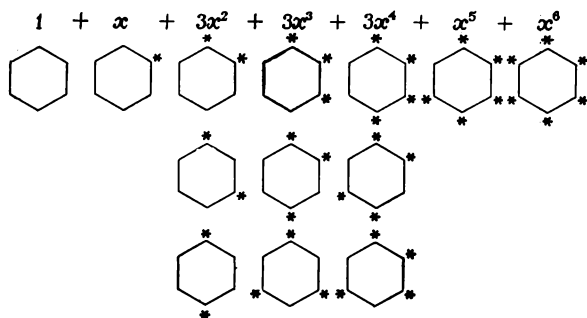
$$1 + x + 3x^2 + 3x^3 + 3x^4 + x^5 + x^6$$

Fig. 51

According to Menshutkin, a molecule is an integral formation and its structure (in the sense adopted by Butlerov) cannot be determined by rigorous physical methods at the contemporary stage of scientific development, and therefore all hypotheses about the way the atoms are bonded should be discarded; the efforts should be concentrated on the study of similarity of properties of compounds. In Menshutkin's opinion, choosing from among the substances with similar properties the simplest ones, one may arrive at the notion of chemical "type" of Gerhardt. "Classifying a compound with a type", pointed out Menshutkin, "implies that the same transformations can be produced with this substance as with the substance taken for the type." We shall not analyse here the strong and weak points of the substitution theory; let us consider only the determination of the number of disubstituted benzene derivatives as proposed by Menshutkin.

He proposed to consider, "without resorting to any structural hypotheses", "the first product of benzene substitution in the order of both the direct and the re-

verse sequence", i.e. to enumerate the "fragments" of CH
as follows:

```
CH CH CH CH CH CX    CX CH CH CH CH CH
 1  2  3  4  5  6     6  5  4  3  2  1
direct sequence of carbon    reverse sequence of carbon
atom enumeration             atom enumeration
```

To determine "which fragments in the direct sequence correspond to the fragments in the reverse sequence", Menshutkin writes the foregoing formulas one under the other

```
CH CH CH CH CH CX
CX CH CH CH CH CH
```

or, in the numerical notation:

$$
\begin{array}{cccccc}
 & \lceil 1 & 2 & 3 & 4 & 5 \rceil\, 6 \\
6 & \lfloor 5 & 4 & 3 & 2 & 1 \rfloor
\end{array}
$$

As a result, the following permutation is obtained:

$$P = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 5 & 4 & 3 & 2 & 1 \end{pmatrix} = (15)\ (24)\ (3) \qquad (40)$$

Further arguments of Menshutkin can be easily interpreted in terms of the permutation group theory. Here the number of cycles in the permutation (40) is equal to the number of disubstituted derivatives, i.e. 3 (ortho-, meta-, and para-), and the digits combined in one cycle indicate the numbers of equivalent positions in a monosubstituted derivative.

Thus, although Menshutkin did not use explicitly the permutation groups (hardly being familiar with them at all), all of his arguments nevertheless are of "permutation group" character.

What was said in no way belittles the importance of

the Butlerov theory but only points out the profound rational content of the substitution theory proposed by Menshutkin*.

Branches of a Topological Tree

Up to now we dealt with counting isomers of various classes of chemical compounds. Not less important, however, is to determine the topological indices characterizing each individual isomer. In the most profoundly studied case of structural isomers of alkanes the problem reduces to the determination of topological parameters defining the extent of branching of their carbon skeleton. Unfortunately, many of the characteristics suggested for this purpose turned out to be insufficiently sensitive to replacing of one isomer by another. In 1977 D. Bonchev (Bulgaria) and N. Trinajstić (Yugoslavia) developed a method of defining the extent of branching of a topological graph (more precisely, a tree) of alkanes; the method is based on the graph theory and the information theory.

Information content. Originally, the term "information" denoted only the data exchanged by people and was of purely qualitative character. During the last 30 years the quantitative theory was elaborated, whose basic aspects will be briefly discussed below.

Suppose a certain system comprises N elements. Then its information content is determined by Shannon's formula:**

$$I = N \log_2 N - \sum_{i=1}^{n} N_i \log_2 N_i,$$

where n is the number of different subsets of elements of the system combined according to some characteristic; N_i

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* A more detailed discussion of this theory and the polemic between Butlerov and Menshutkin can be found in the article by I. S. Dmitriev and L. A. Kartseva "Chemical Structure Theory and Problem of Aromaticity" (*Problems of history and methodology of chemistry*. Issue 2. Ed. by R. B. Dobrotin, Leningrad University Press, 1978, in Russian).

** The American scientist C. Shannon who proposed this formula in 1948 proceeded from the statistical interpretation of the concept of information. However, the elements can be selected not at random but according to some programme. The primary requirement is the existence of a set of elements but not their random character.

is the number of elements in the i-th subset. The information content per one element of the system $(\overline{I})$ is

$$\overline{I} = \frac{I}{N} = - \sum_i p_i \log_2 p_i$$

where $p_i = N_i/N$ is the probability of finding an arbitrarily chosen element of the system in the i-th subset.

The information content is measured in special binary units, bits. According to W. R. Ashby information is a measure of variety of the system. Thus, the set consisting of three spheres of different colours possesses the variety of magnitude three. Every inhomogeneity of distribution of substance or energy in space is also expressed by the quantity I (or $\overline{I}$). In the case of a completely homogeneous system $(N_i = N)$ $I = 0$, in the case of a completely inhomogeneous system $(N_i = 1)$ $I = I_{max} = N \log_2 N$.

In 1955 the US scientist N. Rashevsky introduced a concept of topological information of a graph (I_{top}). His theory is based on subdivision of the set of N vertices of the graph into classes of topologically equivalent vertices. However, the quantity I_{top} turned out to be unsuitable for characterization of branching of alkane's carbon skeleton.

Criterion of branching. The method of Bonchev and Trinajstić is based on the analysis of the matrix D

$$D_1 = \begin{pmatrix} 0 & 1 & 2 & 3 & 4 \\ 1 & 0 & 1 & 2 & 3 \\ 2 & 1 & 0 & 1 & 2 \\ 3 & 2 & 1 & 0 & 1 \\ 4 & 3 & 2 & 1 & 0 \end{pmatrix} \quad D_2 = \begin{pmatrix} 0 & 1 & 2 & 3 & 3 \\ 1 & 0 & 1 & 2 & 2 \\ 2 & 1 & 0 & 1 & 1 \\ 3 & 2 & 1 & 0 & 2 \\ 3 & 2 & 1 & 2 & 0 \end{pmatrix} \quad D_3 = \begin{pmatrix} 0 & 2 & 2 & 2 & 1 \\ 2 & 0 & 2 & 2 & 1 \\ 2 & 2 & 0 & 2 & 1 \\ 2 & 2 & 2 & 0 & 1 \\ 1 & 1 & 1 & 1 & 0 \end{pmatrix}$$
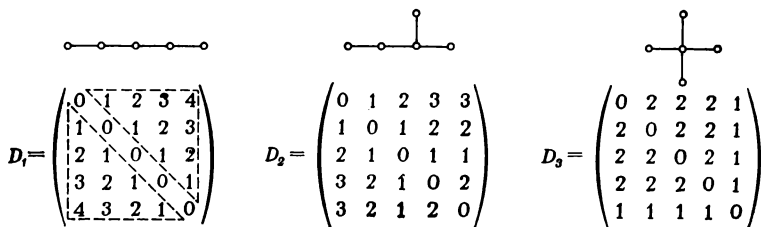
Fig. 52

whose elements d_{kl} represent the shortest distances between the graph's vertices k and l (see Chapter 2 and Fig. 52). With increasing branching the distances in the graph become smaller. If the set containing N^2 elements of the matrix D (N of which are zeros) is partitioned into groups as shown in Table 7, $(m + 1)$ groups are obtained

where $m = (d_{kl})_{max}$. The group containing all zeros is not given in Table 7. The probability for a randomly

Group No.	1	2	3	4
Elements of matrix D_1	{4, 4}	{3, 3, 3, 3}	{2, 2, 2, 2, 2, 2}	{1, 1, 1, 1, 1, 1, 1, 1}

chosen matrix element d_{kl} to be in the i-th group is

$$p_i = 2k_i/N^2,$$

where $2k_i$ is the total number of elements in this group.

Bonchev and Trinajstić introduced the concept of the information on distances within the graph (I_D)

$$I_D = N^2 \log_2 N^2 - N \log_2 N - \sum_{i=1}^{m} 2k_i \log_2 2k_i \qquad (41)$$

and

$$\overline{I}_D = -\frac{1}{N} \log_2 \frac{1}{N} - \sum_{i=1}^{m} \frac{2k_i}{N^2} \log_2 \frac{2k_i}{N^2}. \qquad (42)$$

Noting that each element of the matrix D appears in its lower triangular submatrix the same number of times as in the upper submatrix (namely, k_i times) (Fig. 52), Eqs. (41) and (42) can be replaced by the formulas for one of the above-mentioned submatrices:

$$I'_D = \frac{N(N-1)}{2} \log_2 \frac{N(N-1)}{2} - \sum_{i} k_i \log_2 k_i,$$

$$\overline{I}'_D = -\sum_{i} \frac{k_i}{\frac{N(N-1)}{2}} \log_2 \frac{k_i}{\frac{N(N-1)}{2}},$$

where $\frac{N(N-1)}{2}$ is the total number of upper (or lower) off-diagonal elements in D.

For the topological tree of n-pentane ($N = 5$) we obtain (Fig. 52):

elements of matrix D_1: 1, 2, 3, 4,

values of k_i: 4, 3, 2, 1,

whence

$$\overline{I}'_{D_1} = - \left\{ \frac{4}{10} \log_2 \frac{4}{10} + \frac{3}{10} \log_2 \frac{3}{10} + \right.$$

$$\left. + \frac{2}{10} \log_2 \frac{2}{10} + \frac{1}{10} \log_2 \frac{1}{10} \right\} = 1.84644 \text{ and } I'_{D_1} = 18.4644.$$

Table 8

N	Molecular graph	I'_D	X_{max}
4		8.7549	1.618
		6.0000	1.732
5		18.4644	1.732
		15.2193	1.848
		9.7095	2.000
6		32.2389	1.802
		28.6293	1.902
		27.3842	1.932
		23.4840	2.000
		22.5874	2.074

The quantities I'_D and $\overline{I}'_D$ characterize the inhomogeneity of distribution of distances between vertices of a graph. Their values monotonically decrease as branching of

a molecule increases. Besides, the degree of branching of a carbon skeleton can be compared with the greatest eigenvalue of the topological matrix of a molecule (Table 8).

The quantitative measures of molecular branching derived by Bonchev and Trinajstić are very important since they correlate with many physical and chemical properties of compounds.*

Transition State Topology

Topological methods have found application not only in the investigations of the structure of a molecule but also in the study of mechanisms and rates of chemical

Reaction:

diene dienophile

transition state:
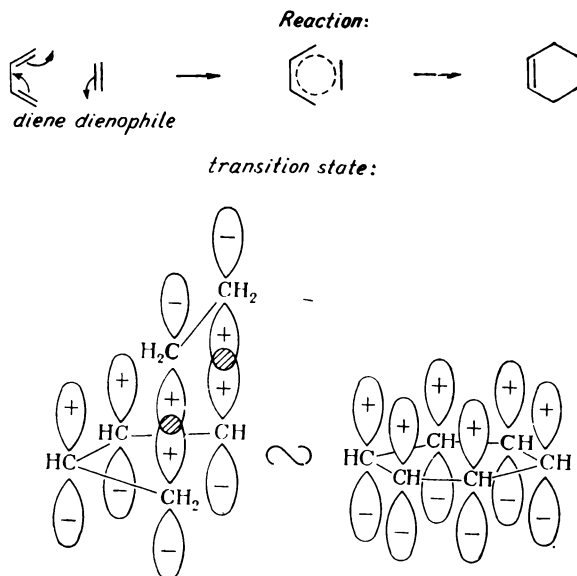
Fig. 53

reactions; the topological theory of concerted reactions may serve as an example.

Evans' rule. In 1938-39 the English chemist M. G. Evans, while studying the Diels-Alder reaction, assumed it

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* For more details see: Bonchev, D., N. Trinajstić, *J. Chem. Phys.* **67**, 10, 4517 (1977).

to be a synchronous process in the course of which six $2p$ carbon AOs (four of diene and two of dienophile) overlap to form a cyclic transition state which is topologically equivalent to benzene * (Fig. 53) and therefore stabilized. In its turn, the process of ethylene dimerization to form cyclobutane must proceed through the anti-aromatic (destabilized) transition state topologically equivalent

Reaction:
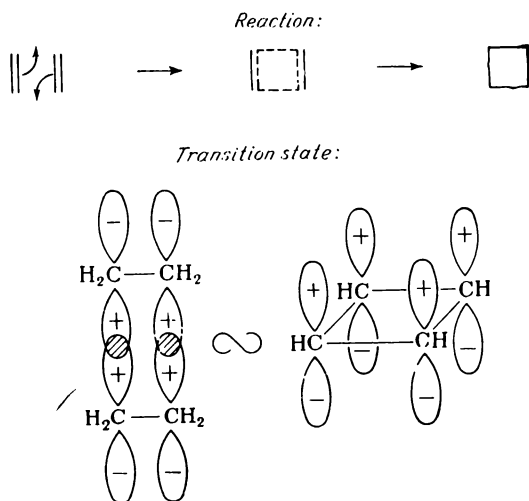
Transition state:

Fig. 54

to cyclobutadiene (Fig. 54); it follows that this reaction is thermally forbidden.

Evans' ideas were developed in 1952 by M. Dewar and in 1966 by H. E. Zimmerman. The synchronous reactions whose transition state can be represented as a cycle to which each constituent atom donates one AO are referred to as *pericyclic*.

Anti-Hückel systems. In 1964 E. Heilbronner considered an unusual type of cyclic π-electron systems with polyene ribbon twisted an odd number of times. The topology of

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* The imaginary connection of overlapping lobes of $2p$-AO transition state results in a curve which is topologically equivalent (homeomorphic) to the curve obtained in the similar analysis of a benzene molecule. The difference between σ and π overlaps of AOs is not taken into consideration.

such a molecule resembles the Möbius band (Fig. 55), a surface first described by the German mathematician J. B. Listing in 1861 and later, in 1863-65, investigated by A. Möbius in full detail. The Möbius band cannot be painted in two colours, one inside and another outside, because it is a one-sided surface. The cyclic π-electron systems possessing the Möbius band topology are referred to as *anti-Hückel*, or *Möbius* systems. In such systems there are an odd number of spots where the AOs of the neighbouring atoms overlap "out of phase". According to
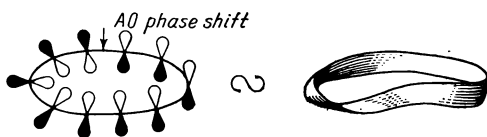
AO phase shift

g. 55

Dewar, "although none of such systems has been obtained so far, it is of great significance to develop a conception to substantiate it. The system in which the AO phase shift is inevitable differs topologically from the system in which such a shift can be avoided.... This difference depends only on the overlap topology of AOs involved in the formation of a delocalized system and is absolutely independent of the MOs that can be composed from those AOs".

Anti-Hückel aromaticity. The aromaticity rules for anti-Hückel systems are opposite to those for conventional (Hückel) systems (Table 9).

Table 9

Number of π-electrons	Topological type of system	Character of system
$4N+2$	Hückel	Aromatic
	Anti-Hückel	Anti-aromatic
$4N$	Hückel	ditto
	Anti-Hückel	Aromatic

Zimmerman's diagrams. For anti-Hückel systems thee MO energies are defined by the following formula:

$$\varepsilon_k = \alpha - 2\beta \cos \left[\frac{2\pi \,(k+1)}{N} \right]$$

$$(k = 0, 1, 2, \ldots, N-1).$$

Accordingly, the mnemonic Frost rule is replaced by the Zimmerman rule for these systems. The latter differs from the former by the position of the inscribed regular polygon (Fig. 56, cf. Fig. 5).
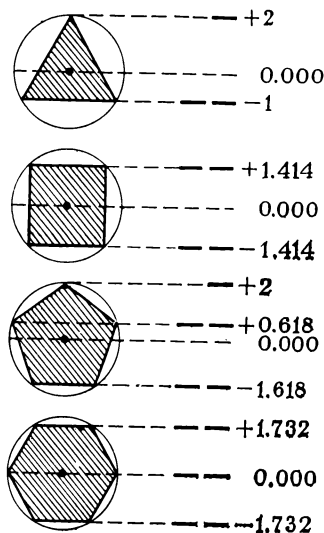
Fig. 56

Evans-Dewar-Zimmerman criterion. In accordance with this criterion the pericyclic reactions proceed through the cyclic transition state of the Hückel topological type if it contains $(4N + 2)$ π-electrons, and through the state with anti-Hückel (Möbius) topology if it contains $4N$ π-electrons.

To determine the topological type of a transition state, one should "walk" around the cycle and count how many times the AO changes its sign*. This sign changes occur-

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* Surely, the cycle can contain not only p AOs.

ring while we move along the same AO are ignored. The Hückel system has an even number of sign changes (including zero), the anti-Hückel one has an odd number.

As an example, let us consider the electrocyclic reaction of cyclobutene to butadiene transformation. The cyclobutene ring can break up either in a conrotatory
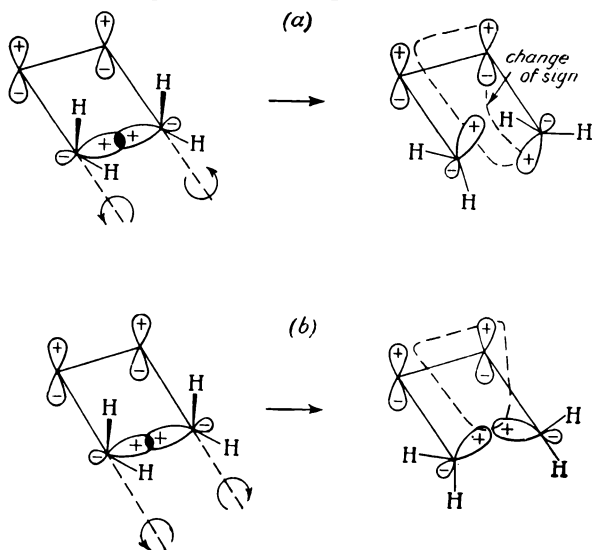
Fig. 57

way (Fig. 57a) or in a disrotatory way (Fig. 57b). In both con- and disrotatory transition states the hybrid AOs of carbon methylene atoms interact not only between themselves but also with p_π AO of the $C = C$ bond, i.e. each carbon atom of the system possesses an AO interacting with AOs of the neighbouring atoms in the ring. Here the four-electron disrotatory transition state relates to the Hückel type and is therefore anti-aromatic whereas the conrotatory state associated with the anti-Hückel topology is aromatic; consequently, the indicated reaction proceeds in a conrotatory way.

Symmetry or topology? For the first time synchronous reactions were theoretically studied by R. B. Woodward and R. Hoffmann on the basis of the orbital symmetry conservation principle formulated by them. This princi-

ple proclaimed initially in the fashion of the Sermon on the Mount was subsequently subjected to a detailed quantum-mechanical analysis. H. Metiu, J. Ross, and G. M. Whitesides* demonstrated that the Woodward-Hoffmann rules emerged from the most simplified treatment in which:

(1) the spin-orbital coupling, the virtual transitions between excited electronic states of reactants and products and the non-Born-Oppenheimer terms are ignored;

(2) the Franck-Condon approximation is used, and

(3) the electronic wave functions are determined by the HMO method. Therefore, a more complete calculation may, in principle, lead to predictions different from those of the Woodward-Hoffmann rules.

In addition, Dewar demonstrated that the classification of pericyclic reactions has nothing to do with symmetry. The nature of the reaction is defined by the AO overlap topology in a pericyclic transition state and not by the MO symmetry.

Conclusion

We have described various applications of the graph theory in chemistry. Surely, much was left outside this book, in particular such problems as topology of molecular potential energy surface, topological aspects of thermodynamics of heterogeneous equilibrium systems, the graph theory and coding of chemical information. However, even what was said suggests the fundamental importance of topological ideas and methods. The primary areas of chemical science in which the graph-theoretical and topological methods are employed are shown in Fig. 58.

The topological ideas play an important part in stereochemistry. Here is one fairly indicative example. In the latest chemical literature the problems associated with the concepts of stereochemical configuration, conformation, and chirality have been extensively discussed. In particular, the concept of configuration was shown to be applicable only to chiral molecules, i.e. to such mole-

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* H. Metiu, J. Ross, G. M. Whitesides. *A Basis for Orbital Symmetry Rules.*—Angew. Chem. Intern. Edition in English, **18**, 5, 377 (1979).

cules that cannot be superimposed upon their mirror images by translation and rotation. Hence, various types of molecular deformations proceeding both with a change in configuration and with the preservation of the latter were considered. Of special interest is the first type of
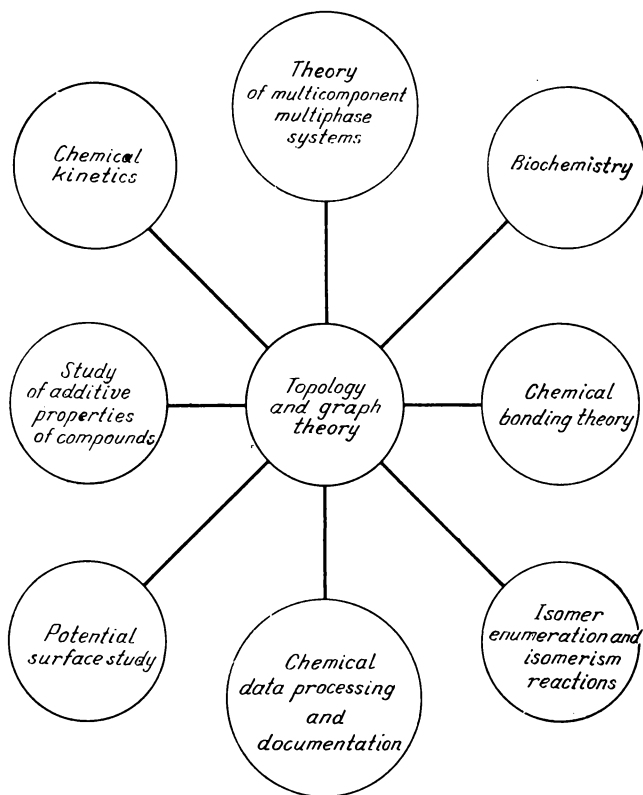

Fig. 58

transformation going either via chiral (e. g. Berry's pseudorotation for a trigonal bipyramid, see Fig. 47) or achiral (e. g. in the diagonal twist) intermediate. In either case the topological pattern] of a molecule changes. When considering such intramolecular motions it should be taken into account that a molecule may possess some

singular points; this fact makes it necessary to introduce certain corrections into the strictly geometrical consideration. For example, let us look at a molecule of symmetry T_d. As distinct from the tetrahedron treated in a strict geometrical sense (and we remind the reader that in that sense all tetrahedrons are homeomorphic), a tetrahedral molecule, as a rule, possesses a singular point, the point at which the central atom is located. When such a tetrahedral structure is transformed into a disphenoid one and then into a tetragonal pyramid, this singular point (the central atom) first comes out to the surface of the disphenoid and then becomes the pyramid's vertex. This and other similar examples have brought about the concept of *molecular topological form* which is understood as a topological pattern in combination with singular points of the molecule. The molecular topological form was shown to be unique for every molecule*. If the molecular topological form is retained in the process of a conformational transition, the conformations associated with that transition are of the same configuration type. In other words, the configuration remains unchanged for a certain set of molecular conformations. If we now take into account that the concept of configuration (the absolute configuration is meant) is meaningful only for chiral molecules, the following definition can be given: the stereochemical (absolute) configuration is an inherent invariant of a chiral molecular topological form.

Such an approach turned out to be very fruitful in theoretical stereochemistry. In particular, it helps to establish a topological resemblance between various chemical structures. For example, it can be shown that the conformational transition between the eclipsed and staggered conformations of an ethane molecule is similar to the trigonal twist in an octahedron resulting in a trigonal prism formation. In these extreme conformations the molecular topological form of ethane reduces to a trigonal prism and a trigonal antiprism possessing two internal singular points occupied by carbon atoms.

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* The readers interested in problems of chemical topology and application of topological ideas to stereochemistry are advised to look through the remarkable book by V. I. Sokolov *Introduction to Theoretical Stereochemistry*, Moscow, 1979 (in Russian).

At present, in stereochemistry, as in other areas of chemistry, ever increasingly important for traditional chemical problems become such unusual (but on the second thought, quite natural) mathematical disciplines as the set theory, topology, the group theory, mathematical logic, the information theory, etc. Here we witness the *nonquantitative mathematization of knowledge*, so characteristic for modern natural sciences.

Recommended Literature

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2. F. Harary, *Graph Theory*, Addison-Wesley Reading, Mass., 1972.
3. D. H. Rouvray, *Graph Theory in Chemistry*, R.I.C. Reviews, Vol. 4, No. 2, 1971.
4. I. Gutman, N. Trinajstić, *Graph Theory and Molecular Orbitals*, Topics Curr. Chem., Vol. 42, 1973.

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Suggested Further Readings

Symmetry in the World of Molecules

I. DMITRIEV, D. Sc.

The fascinating and mysterious phenomenon of symmetry has been thrilling a man from time immemorial. More than once the symmetry theory helped to penetrate the nature's secrets.
The booklet tells how the concept of symmetry can be applied in quantum chemistry. Due to this concept much information on the electronic structure and other properties of a molecule can be obtained without resorting to the solution of complex equations. The author presents the main principles and touches upon some interesting results obtained in recent years.
The booklet is distinguished with the simplicity of language so that no special mathematical training is required to read it. It is intended for experimental chemists, college teachers and students as well as high school students interested in the modern theory of chemical bond and the structure of molecules.

From Crystal to Solution

G. KRESTOV, D. Sc., and V. KOBENIN, Cand. Sc.

How are electrolyte solutions formed, and what effect does the nature of the electrolyte and the solvent produce on this process? In what state is the ion present in solution? What is the structure of the solution and the solvent, water in particular? These and many other questions are discussed in this booklet written in popular and, at the same time, strictly scientific language. The booklet is intended for school undergraduates, students, and teachers, as well as for all those who strive to widen their knowledge in chemistry.

Elements of Game Theory

Ye. VENTTSEL, D. Sc.

This book presents in a popular manner the elements of game theory—the mathematical study of conflict situations whose purpose is to work out recommendations for a rational behaviour of each of the participants of a conflict situation. Some methods for solving matrix games are given. There are but few proofs in the book, the basic propositions of the theory being illustrated by worked examples. Various "conflict situations" are considered. To read the book, it is sufficient to be familiar with the elements of probability theory and those of calculus.

The book is intended to disseminate the ideas of game theory which is of wide practical application in economics and the art of war.

How Did They Discover Chemical Elements

D. TRIFONOV and V. TRIFONOV

This book deals with the history of the discovery of chemical elements from ancient times to the present day. In the course of writing this history, the authors relate the most important regularities in the process of discovery of elements, the role of various methods of study; they throw light upon the contribution of scientists from different countries in developing the science about elements. This book is a supplement to school text-books of chemistry and could be valuable to pupils in their independent studies.